A STUDY OF THE PYROLYSIS OF POLY(ETHYLENE TEREPHTHALATE) BY MEANS OF MODEL SYSTEMS.

THESIS

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Publications.

Communications concerning part of this work have been published as follows:

" The Pyrolysis of Vinyl Benzoate ", R.J.P. Allan and P.D. Ritchie, Chemistry and Industry, 1953, page 747.

" Model Systems for the Pyrolysis of Poly(ethylene Terephthalate) and Allied Polyesters ", R.J.P. Allan, R.L. Forman, and P.D. Ritchie, Journal of the Chemical Society, 1955, pages 2717 - 2725.

I N D E X

List of compounds referred to in the text, and numbers allotted to them.

I	poly(ethylene terephthalate)
II	ethylene dibenzoate
III	vinyl benzoate
IV	benzoylacetaldehyde
V	ethylene
VI	ethylidene dibenzoate
VII	2-benzoyloxyethyl terephthalate
VIII	4-acetylbenzoic acid
IX	cyclohex-1-enyl benzoate
X	2-benzoylcyclohexanone
XI	acetylacetone
XII	trimethylene dibenzoate
XIII	allyl benzoate
XIV	benzaldehyde
XV	acrolein (acraldehyde)
XVI	propylene diacetate
XVII	propylene dibenzoate
XVIII	allyl acetate
XIX	benzoic acid
XX	benzoic anhydride
XXI	acetaldehyde
XXII	acetophenone
XXIII	styrene

XXIV	acetylene
XXV	terephthalic acid
XXVI	allylbenzene
XXVII	2-benzoyloxyethyl vinyl terephthalate
XXVIII	ethylene dibenzoate-4-carboxylic acid
XXIX	vinyl terephthalate (i.e., divinyl terephthalate)
XXX	vinyl hydrogen terephthalate
XXXI	vinyl 4-acetylbenzoate
XXXII	1:4-diacetylbenzene
XXXIII	benzoylacetaldehyde-4-carboxylic acid
XXXIV	dodecahydrotriphenylene
XXXV	isopropenyl acetate
XXXVI	propenyl acetate

Summary.

The increasing importance of poly(ethylene terephthalate), " Terylene ", has made it necessary to have a fuller understanding of the manner in which this polyester undergoes thermal breakdown. Several investigations into this have already been reported, but in no case has it been possible to produce sufficient evidence from which the actual mechanism of breakdown might be deduced. Furthermore, there is even lacking a proper understanding of the manner of breakdown of simpler esters, particularily those that might be postulated as holding an intermediate position in the general plan of polyester decomposition. It was clear, therefore, that any further advance in this subject must be restricted to hypothesis until a fuller investigation had been undertaken. It was also clear that this investigation would have to be concerned with simpler esters, which were related to the polyester, and which contained the same groupings.

By way of providing this basic knowledge, a series of model compounds has been prepared, and subjected to pyrolysis under varying conditions. These compounds have been chosen because of the relationship they bear to the polyester itself and, in several instances, to products that might be postulated as coming from the polyester breakdown. It has also been within the scope of this work to study the pyrolysis

of several other model compounds which were not directly related to the polyester. These were compounds which contained slight structural modification to the original model compounds, thereby illustrating whether the behaviour observed in the original model was general or not.

As a result of this work it has been possible to observe and explain several reactions in the thermal breakdown of esters which had not hitherto been reported. These findings have included (1) the thermal rearrangement of vinyl esters to a β-ketoaldehyde, which then undergoes decarbonylation to a methyl ketone, (2) the reversibility of thermal rearrangement of alkenyl esters, (3) the thermal disproportionation of diesters, (4) the decarboxylation of esters, and (5) the orientation of proton elimination in alkylene diesters. Several of these results can now be applied successfully to explain the reported findings from earlier studies of the breakdown of the polyester, many of which at that time appeared to be quite anomalous.

Introduction.

The Pyrolysis of Esters.

The pyrolysis of model compounds representing units of the linear polyester poly(ethylene terephthalate) has been found to include examples of every type of ester thermal decomposition which had hitherto been described. In order, therefore, to exemplify the relation between these known examples, and the present results, a detailed survey of all the known routes of the pyrolysis of carboxylic esters is given below.

1.1.1 : General.

The pyrolysis of carboxylic esters has been extensively studied, and a survey of the literature (1) indicates that, as a general rule, esters of the formula

$$R.CO.O.CH_2CH_2.R'$$

pyrolyse to give

$$R.COOH + CH_2{:}CHR'$$

this scission involving the migration of a β-hydrogen atom. However, while this is frequently the route which gives the major products, it is now clearly recognised that there are several other possible routes which may compete with, or even predominate over, the above type of scission. It is also important to note that secondary pyrolysis of the products formed by the primary, or first stage of decomposition, can

occur, and these products should not be confused with, or regarded as products of competing primary routes.

A survey of the literature indicates that in many cases only those major products which were readily identified were reported, and this frequently without regard to or consideration of the manner of their production. There are thus many seemingly conflicting results in the literature. It is, however, often possible to provide a satisfactory explanation for such results by a consideration of either the non-identification or the further pyrolysis of the concomitant products, in which case the evidence may be completely fragmentary. It is therefore quite desirable that every advanced aid available be employed for the analysis of the products of a pyrolysis, and every product should be regarded as a valuable piece of evidence, quite necessary for the full understanding of the complete pattern of thermal decomposition.

In general, the determining factor for the route or routes of pyrolysis will be the composition and construction of the molecule, and the polarity and steric effect of the substituent groups R and R', together with the lability of the available α- and β-hydrogen atoms, will exert their influence to varying degrees on the thermal stability of the molecule.

Using the existing knowledge and the many reported examples of ester pyrolysis, it is possible to produce a classification which will cover, almost completely, the routes of breakdown

which may obtain in the pyrolysis of most carboxylic esters. This classification is given below, and the nomenclature given indicates the effective point of scission:

(i) Alkyl-oxygen scission, type A, where the split occurs between the ether oxygen of the ester group and the alkyl, alkylene, or alkenyl group.

(ii) Acyl-oxygen scission, type B, where the split occurs between the carbonyl group and the ether oxygen of the ester group.

(iii) Decarbonylation, decarboxylation, type C. Pyrolytic elimination of carbon monoxide or carbon dioxide from the ester molecule.

(iv) Disproportionation, type D, where, for example, two identical molecules yield two different molecules of greater symmetry.

(v) Rearrangement, type R, with the formation of an isomer, which may or may not decompose into further products.

These various types of ester scission are exemplified below, under their respective headings.

1.1.2 : Alkyl-oxygen scission, type A.

This type may be further classified into alkyl- and alkylene-oxygen scission (type A^1) and alkenyl-oxygen scission (A^2),

$$R.CO_2.CH_2CH_2.R' \longrightarrow R.CO_2H + CH_2{:}CHR' \quad ...A^1$$

$$R.CO_2.CH{:}CH.R' \longrightarrow R.CO_2H + CH{:}CR' \quad ...A^2$$

Type A^1.

The pyrolysis of ethyl acetate has been reported by Oppenheim and Precht (2) to yield ethylene and acetic acid, and there have been a great number of similar reactions reported since then (3), and its use as a means of synthesis of unsaturated compounds is now well established (4). A comparative study of tert.-, sec.-, and n-alkyl carboxylates by Hurd and Blunck (5) has shown that the stability of the ester decreases as the number of available β-hydrogen atoms increases. However, as the stability of esters in an homologous series increases, so does the complexity of the pyrolysis, and the number of competing routes. Thus tert.-butyl acetate pyrolyses simply, and at a relatively low temperature, to the acid and olefin, whereas, isopropyl acetate and ethyl acetate respectively require higher temperatures and give more complex pyrolysates, thus:

$AcO.CMe_3 \xrightarrow{360^\circ}$ AcOH + $CH_2{:}CMe_2$ (sole products) ...A^1

$AcO.CHMe_2 \xrightarrow{430\text{-}460^\circ}$ AcOH + $CH_2{:}CHMe$ (main products) ...A^1
+ Me.CHO + $COMe_2$ + CO (by-products)

$AcO.CH_2.Me \xrightarrow{525\text{-}530^\circ}$ AcOH + $CH_2{:}CH_2$ (main products) ...A^1
+ Me.CHO + H.CHO + Ac_2O
+ CH_4 + H_2 + CO + $CH_2{:}CO$ (by-products)

This result is clearly associated with the number of β-hydrogen

atoms, and the simplicity of pyrolysis of tert.-alkyl carboxylates has enabled Rudy and Fugassi (6) and Warwick and Fugassi (7) to carry out quantitative kinetic studies on tert.-butyl acetate and propionate respectively. Unfortunately, however, comparable simplicity of ester pyrolysis is rare, thus making quantitative study generally too complicated to be of any value. In the pyrolyses above where by-products have been found, these can be related to competing acyl-oxygen scission (type B), or to secondary reactions of products of these competing routes.

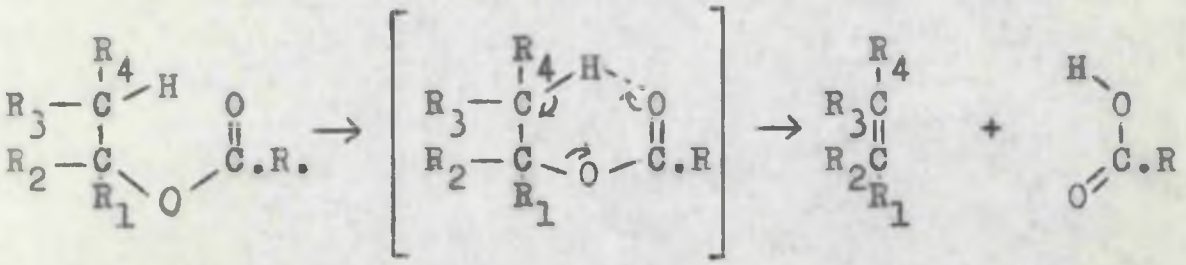
The relative thermal stability of alkyl esters has been confirmed by van Pelt and Wibaut (8), and also Rehburg and Fisher (9), who have suggested that the esters of primary alcohols decompose at ca. 500-525°, and esters of secondary alcohols at ca. 450°. They also state that no displacement of the double bond or change in the carbon skeleton accompanies the pyrolytic formation of alkenes. Houtman, Steenis, and Heertjes (10), however, have been able to detect small amounts of double bond isomerisation, thus:

$$CH_3CH_2CH_2CH_2OAc \longrightarrow \underset{1.5\ \%}{CH_3.CH{:}CH.CH_3} + CH_3CH_2CH{:}CH_2 + AcOH$$

However, because the formation of isomers is promoted by an increase in the contact time, they have concluded that this is a secondary reaction.

It has been stated above that alkyl-oxygen scission is dependent on the presence of β-hydrogen atoms, and by way of

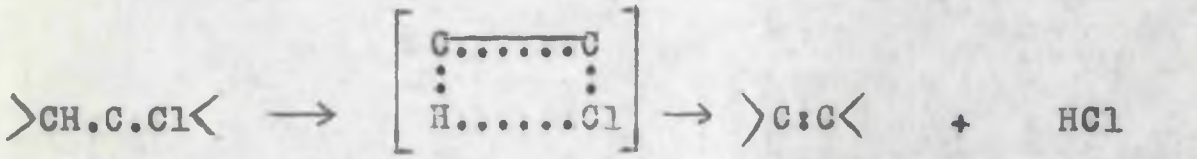
explaining this method of scission, Hurd and Blunck (5) have postulated an hydrogen-bonded six-membered chelate ring, thus:



Houtman et al. (10) criticised the postulated hydrogen-bonding of this chelate ring, and they have preferred to call the bonding " mutual interaction ". Otherwise, however, Houtman et al. do not disfavour this chelate ring theory, which gives an explanation for the absence of any major carbon-skeleton isomerisation, and they suggest that the difference in stability of tert.-, sec.-, and n- alkyl carboxylates is caused by variation in the relative bond strengths of the C-O and C-H bonds. Thus in tertiary esters (e.g., tert.-butyl, $R_1 = R_2 = Me$ and $R_3 = R_4 = H$), the C-O bond breaks easily, and so the ester pyrolyses simply, and at a lower temperature. However, in secondary ($R_1 = Me$, $R_2 = H$) and primary ($R_1 = R_2 = H$) esters, the C-O bond becomes stronger, and reaction occurs at higher temperatures (particularily in primary esters). Alexander and Mudrak (11) have also favoured a cyclic transition-state complex in their work on xanthates and acetates, although they state that other paths of the decomposition are possible. The xanthate esters have been further studied by Stevens and Richmond (12) who also postulate hydrogen-bonding prior to proton

elimination, and other evidence for this mechanism of pyrolysis of esters has been produced by Arnold, Smith,and Dodson (13).

Barton (14) has considered a comparable problem, the cis elimination of hydrogen chloride thermally from chlorohydrocarbons, and for this he has preferred to postulate a four-membered cyclic transition stage :



This postulate is, of course, quite compatible with the six-membered ring theory for alkyl carboxylates, since the latter involve two more atoms than the chlorohydrocarbons. Barton has also found that the homolytic bond dissociation energies of C-X bonds (where X = H,OH,Cl,Br,I, etc.) diminish markedly in the series primary, secondary, tertiary. Thus unimolecular elimination of H-X should proceed with decreasing activation energy in the series :

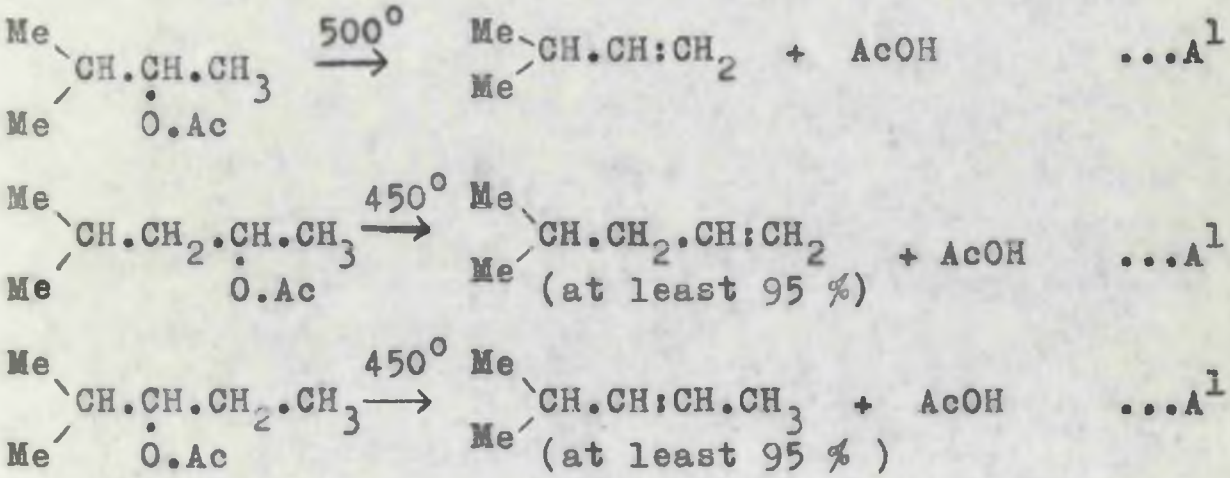
$$-C\text{-}X \text{ (primary)} \;\rangle\; >C\text{-}X \text{ (secondary)} \;\rangle\; \rightarrow C\text{-}X \text{ (tertiary)}$$

In support of this he has found the activation energies of the following to decrease in this order :

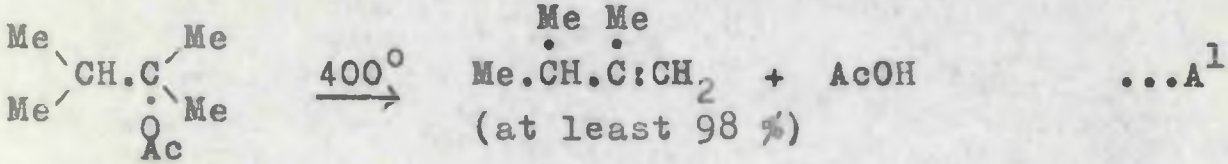
$Me.CH_2.Cl$	E_A	= 60.8 kcal
$Me_2CH.Cl$	E_A	= 50.0 kcal
$Me_3C.Cl$	E_A	= 41.4 kcal

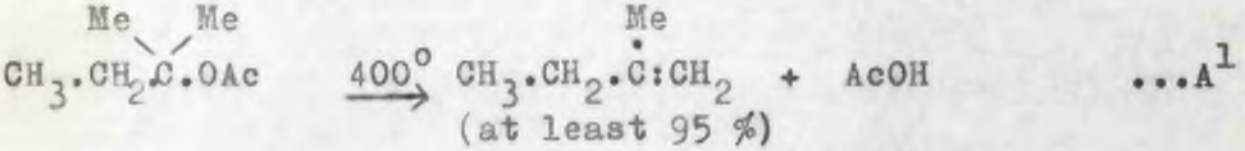
In the pyrolysis of tert.-alkyl carboxylates, or similar

branched alkyl carboxylates, there is no question of the orientation of proton elimination, since all the available β-hydrogen atoms come from equivalent methyl groups. However, in esters where the source of β-hydrogen atoms may lie equally in the methyl, methylene, or methylidyne groups, it has been found that it need not be the supposedly more labile proton which is eliminated. Thus, Bailey and King (15) have found that the single olefin produced on pyrolysis of secondary esters with differently substituted β-carbon atoms invariably corresponds to the exclusive elimination of the proton of that carbon atom which carries the greatest number of β-hydrogen atoms, thus :

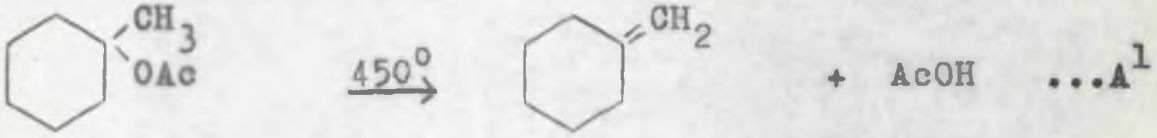


Furthermore, Bailey, Hewitt, and King (16) have extended these studies to tertiary esters, and found the same rule to hold, thus :





Perhaps the most interesting example afforded by Bailey *et al.* (16) is the pyrolysis of 1-methylcyclohexyl acetate, which gives as its sole product, methylenecyclohexane, thus :

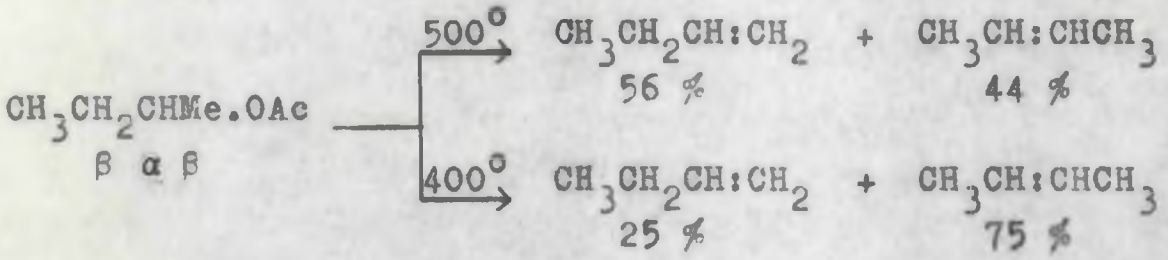


This is a particularily good example of the selectiveness of this reaction, since the alternative product, 1-methylcyclohexene, is considered to have a less strained structure. This has been illustrated by Birch, Kon, and Norris (17), who have shown that a double bond is more stable endocyclic to a cyclohexane than exocyclic to it.

In none of the above examples were any of the isomeric olefins found concurrently. This result is in parallel agreement to Hofmann's Rule (18),(which states that where a quaternary ammonium hydroxide containing different primary alkyl radicals is decomposed, the olefin formed is that which carries the smallest number of alkyl substituents) but is rather surprising in view of the known lability of an hydrogen atom on a tertiary carbon atom. (Thus, for example, in contrast to methane, trimethyl methane may be oxidised or nitrated.) It is perhaps significant that Bailey *et al.* (15, 16) took

particular care that the conditions of their pyrolyses were such that no carbonisation took place. The necessity of this, if double bond isomerisation is to be avoided, has been clearly demonstrated by several workers (inter al., Bailey and Rosenberg, 19).

Houtman et al. (10) appear to have considered this aspect, but, whereas Bailey et al. found pyrolysis to yield almost exclusively the single alkene, the former workers have found that both of the two possible alkenes are formed on the pyrolysis of sec.-butyl acetate, thus :



They have stated that increased temperatures did not appreciably change these relative quantities, and from this they have deduced that no equilibrium mixture is formed, but that the formation of the respective amounts is determined by the ratio of the rates at which the two β-hydrogen atoms are split off.

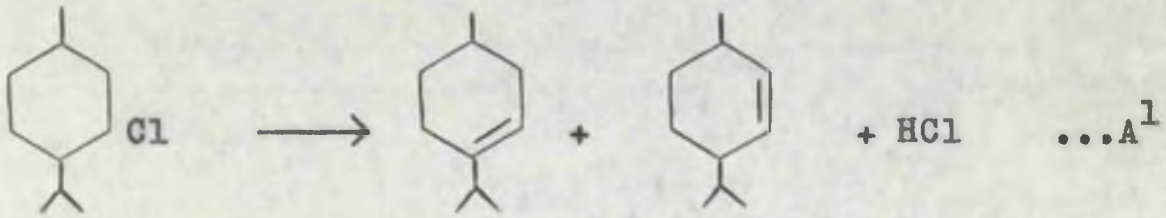
While this result is in complete contrast to the results of Bailey et al., it should be noted that Houtman et al. pyrolysed sec.-butyl acetate (a) at 470° over "clean" glass-wool with a contact time of 144 seconds, and (b) at 460° over "used" glass-wool with a contact time of 90 seconds, and in both cases

found the same proportions of isomeric butenes. This suggests that reaction (a) also took place over carbonised glass-wool, and was therefore heterogeneous, in which case double-bond isomerisation is very likely to take place. In agreement with Bailey *et al.*, Houtman *et al.* have concluded that the ease with which a proton is lost is in the decreasing order,

$$-CH_3 \quad \rangle \quad \rangle CH_2 \quad \rangle \quad \rightarrow CH$$

which they suggest as the reason for the relatively high stability of *iso*butyl acetate, which, they state, decomposes at *ca.* 520°.

The rules regarding orientation of elimination which have been discussed above are not, however, completely specific, as has been shown by the work on the pyrolysis of the menthyl esters. Barton *et al.*, (14, 20) has shown that (-)-menthyl chloride decomposes into a mixture of menthenes, thus :



...A[1]

75-70 % 25-20 %

These authors have also shown (21) that (-)-menthyl benzoate yields 64-68 % of the (+)-p-3-menthene and 36-32 % of the (+)-p-2-menthene, while McNiven and Read (22) have demonstrated that (-)-menthyl acetate yields 65.5 % and 34 % of the two menthenes respectively. Clearly then, in all these examples, the

proton is being abstracted preferentially from a tertiary carbon atom in relation to a secondary carbon atom. It is worthy of note that the above results are in agreement with Saytzeff's Rule (18, 23) (which states that of the isomeric olefins which can be formed from a tertiary or secondary alkyl halide by elimination in the different branches of the alkyl chain, the one actually produced in the greatest proportion is determined by the condition that the eliminated hydrogen atom is lost preferentially from that carbon which bears the smallest number of hydrogen atoms). It is also of interest that Hughes, Ingold, et al., (18) have pointed out that both Hofmann's and Saytzeff's Rules, contradictory as they are, may co-exist, entirely dependent on the circumstances and conditions of the reaction.

It has been found by Bilger and Hibbert (3) that esters without a β-hydrogen atom do not decompose within the range normally adequate for esters possessing a β-hydrogen atom. Thus they found that methyl and benzyl acetate, and also methyl and benzyl benzoate were stable at 500°. However, these esters can undergo a quasi-alkyl-oxygen scission, to yield, amongst other products, ethylene and the appropriate acid. Thus Peytral (24) found methyl acetate to pyrolyse at 1100°. These reactions, however, cannot be of the same mechanism as a true A^1 pyrolysis, as they apparently involve a radical mechanism, probably via a transient diradical (e.g., $CR_1R_2<$).

Type A^2.

Very little difference exists between types A^1 and A^2 in mechanism, and examples of type A^2 are necessarily much fewer. In general, this is probably because the sole available β-hydrogen atom comes from a methylidyne group. While the vinyl esters serve as examples for this type of scission, it should be noted that theoretically the allyl esters may behave similarily, since they also contain a β-methylidyne group.

1.1.3 : Acyl-oxygen scission, type B.

When an alkyl carboxylate undergoes an acyl-oxygen scission, the migration of an α-hydrogen atom is involved, and this proton may be supplied from either the acyl or alkyl radical, thus:

$$R.CH_2COO.CH_2.R' \longrightarrow (\underset{\alpha}{RCH_2}CO. + R'\underset{\alpha}{CH_2}O.)$$

There are therefore two modes of scission which are distinct, since the products of each are different. Thus, if the proton comes from the alkyl radical, the products are two carbonyl compounds,

$$R.CH_2.CO\overset{\downarrow}{\underset{\alpha}{O}}.CH_2.R' \longrightarrow R.CH_2.CHO + R'CHO \quad \ldots B^2$$

whereas, if the proton comes from the acyl radical, the products

are a keten and a hydroxyl compound:

$$R.\overset{\alpha}{CH_2}.CO.O.CH_2.R' \longrightarrow R.CH{:}C{:}O + R.CH_2OH \quad \ldots B^1$$

Type B^2.

Generally speaking, esters which do not possess a β-hydrogen atom are more thermostable, and, when they do decompose, acyl-oxygen scission is often the major route. Thus, methyl formate pyrolyses at 1150° to yield a small amount of formaldehyde, together with large amounts of hydrogen and carbon monoxide (Muller and Peytral, 25, also Peytral, 26), thus:

$$H.CO.O.CH_3 \xrightarrow{1150^\circ} 2\ HCHO \quad \ldots B^2$$

$$HCHO \longrightarrow H_2 + CO$$

Methyl acetate has been shown by Peytral (24) to decompose by two routes, an acyl-oxygen scission, and a quasi-alkyl-oxygen scission (as mentioned above), thus:

$$CH_3.COO.CH_3 \xrightarrow{1100^\circ} \begin{cases} \longrightarrow CH_3COOH + \tfrac{1}{2}\ CH_2{:}CH_2 & \ldots A^1\ \underline{\text{quasi}}- \\ \longrightarrow [CH_3CHO + HCHO] & \ldots B^2 \end{cases}$$

$$\longrightarrow 2\ CO + CH_4 + H_2$$

In contrast to type A scissions, it is not really possible to postulate any single mechanism which is satisfactory, nor does the route proceed via any conceivable cyclic intermediate

(e.g., vide Bilger and Hibbert, 3). Thus, Engler and Low (27) pyrolysed methyl phenylacetate in a sealed tube at 360°, finding toluene and methanol, together with carbon monoxide, carbon dioxide, and methane. Their interpretation of this reaction was as follows :

$$Ph.CH_2COOO.CH_3 \longrightarrow \underset{\downarrow}{[PhCH_2CHO]} + \underset{\downarrow}{CH_2O} \quad \ldots B^2$$
$$PhCH_3 + CO \quad H_2 + CO$$

Hurd and Blunck (5) repeated this work, carrying out the pyrolysis at 625° in the vapour-phase, and they have reported the following products (shown in molar ratios),

formaldehyde,1 ; toluene,1.7 ; benzaldehyde,4.7,

together with 53 % carbon monoxide, 19 % hydrogen, 16 % ethylene, and also methane and carbon dioxide. By way of explaining these products, Hurd and Blunck have postulated a radical mechanism, initially involving the loss of a proton, thus:

$$Ph.CH_2COO.CH_3 \longrightarrow Ph.\overset{\cdot\cdot}{\underset{\cdot\cdot}{\overset{H}{C}}}.COO.CH_3 + H^+$$
$$Ph.\overset{\cdot\cdot}{\underset{\cdot\cdot}{\overset{H}{C}}} + .COO.CH_3$$

The C-C bond which breaks is in the β-position to the unsaturation of the phenyl ring, and it therefore possesses an instability not found in acetic esters (Hurd and Bollman, 28).

Since the benzylidene radical does not possess a complete octet on the α-carbon atom, it unites readily with a molecule which possesses unshared electrons, e.g., any oxygen compound. The carbomethoxy radical decomposes,

$$.COO.CH_3 \longrightarrow CO + .OCH_3 \quad \text{or} \quad CO_2 + .CH_3$$

and, fulfilling the above conditions, the reaction proceeds:

$$Ph\text{-}\dot{C}H + :O{=}C{=}O: \longrightarrow Ph.\dot{C}H\text{-}\overset{-}{O}\text{-}\overset{+}{C}{=}O: \longrightarrow Ph.\dot{C}H{=}O: + CO$$

Ethyl phenylacetate decomposes at a much lower temperature (Hurd and Blunck, 5), and does not yield benzaldehyde, which confirms the high temperature requirements of a radical reaction such as shown above.

Type B[1].

This second mode of acyl-oxygen scission is much less common, but a good example has been shown by Hurd and Blunck (5) in the pyrolysis of phenyl acetate, since this compound does not have any available α-hydrogen atoms on the 'alkyl' radical.

$$CH_3COOPh \xrightarrow{625\text{-}45^{\circ}} CH_2{:}CO + PhOH \quad \text{(exclusively)} \qquad \ldots B$$

The same authors have afforded another example of this scission in the pyrolysis of ethyl acetate, (this example has been referred to in a previous section) thus:

$$AcO.Et \xrightarrow{525^{o}} \begin{cases} AcOH + CH_2{:}CH_2 & \ldots A^1 \\ CH_3CHO + CH_3CHO & \ldots B^2 \\ CH_2{:}CO + EtOH & \ldots B^1 \end{cases}$$

Several other products are mentioned, but these may all be attributed to the further pyrolysis of the above products.

1.1.4 : Decarbonylation, decarboxylation, type C.

Decarbonylation, type C^1.

This type of pyrolysis is most frequently found in aldehydes, or compounds containing an aldehydic group. Thus, Nef (29) has found that acetaldehyde and propionaldehyde suffer primary decomposition to carbon monoxide and the appropriate hydrocarbon. This reaction is general to most aldehydes. Esters containing a keto-type carbonyl group may also pyrolyse with the elimination of carbon monoxide, e.g., ethyl pyruvate:

$$Me.CO.COOO.Et \xrightarrow{100\text{-}130^{o}} CO + \underset{\text{(traces)}}{CO_2} \qquad \ldots C^1$$

This reaction has been studied by Calvin and Lemman (30), who have introduced the isotope (^{14}C), and they have found that it is not the keto group which is eliminated, but rather the ester

carbonyl:

$$Me.{}^{14}CO.COOO.Et \xrightarrow{100\text{-}130^{\circ}} CO \ (90\ \%) + CO_2 \ (\text{traces}) + \text{by-products containing all the radioactive } ({}^{14}C). \quad \ldots C^1$$

Roberts, Smith, and Lee (31) have used a similar technique in the pyrolysis of diphenyl triketone, showing that the middle carbonyl is eliminated, and not either of its neighbours:

$$Ph.{}^{14}CO.CO.CO.Ph \xrightarrow{AlCl_3} CO + Ph.{}^{14}CO.CO.Ph \quad \ldots C^1$$

It is apparent from these last two results that the eliminated molecule need not come from what might appear to be the more probable position.

Decarboxylation, type C^2.

The thermal decarboxylation of carboxylic esters is a reaction which hitherto has been reported only very rarely, although, of course, the decarboxylation of carboxylic acids is a very general reaction. As a result, there are only a few examples of ester decarboxylation in the literature, and, because several new examples have been found in this present work, those few are of considerable interest.

Phenyl cinnamate has been reported as the decarboxylation product of phenyl maleate (Bischoff and v. Hedenstein, 32) and of phenyl fumarate (Anschutz and Wurtz, 33), on slow

distillation at ca. 300°,

$$Ph.OCO.CH{:}CH.COO.Ph \longrightarrow CO_2 + Ph.CH{:}CH.COO.Ph \quad ...C^2$$

and thereafter, phenyl cinnamate itself undergoes decarboxylation to trans-stilbene (vide also Skraup and Beng, 34):

$$Ph.CH{:}CH.COO.Ph \longrightarrow CO_2 + Ph.CH{:}CH.Ph \quad ...C^2$$

This reaction of aryl cinnamates has been further investigated by Anschutz (35) who has found it to be a general reaction, where Ar = p-tolyl, β-naphthyl, p-chlorophenyl, and p-bromophenyl:

$$Ph.CH{:}CH.COO.Ar \longrightarrow CO_2 + Ph.CH{:}CH.Ar \quad ...C^2$$

Another example has been afforded by Pilachione et al. (36) who have shown that styrene is produced from the pyrolysis of phenyl α-acetoxypropionate, in which the main product is phenyl acrylate (cf. 4), which then probably decarboxylates:

$$AcO.CH.Me.COO.Ph \xrightarrow{500\text{-}550^\circ} AcOH + CH_2{:}CH.COO.Ph \quad ...C^1$$

$$CH_2{:}CH.COO.Ph \longrightarrow CO_2 + CH_2{:}CH.Ph \quad ...C^2$$

Unfortunately, very little is known about this type of pyrolysis, which makes it impossible to predict or suggest the mechanism by which the reaction proceeds.

1.1.5 : Disproportionation, type D.

Disproportionation has been recognised for a long time as a characteristic organic reaction. Thus it was shown by Cannizzaro

in 1853 that the action of concentrated sodium or potassium hydroxide on certain aldehydes (those which have no α-hydrogen atom, and, generally, aromatic aldehydes) brings about the oxidation of one molecule of the aldehyde at the expense of the other which is reduced. There is also strong evidence for disproportionation as a reaction undergone by free radicals in the gaseous state. This has been investigated by many workers (inter al., Geddes and Mack, 37, also Steacie, 38) who claim this type of reaction for radicals more complex than the methyl radical (CH_3.). Thus it has been postulated that the ethyl radical can be the source of ethane and ethylene:

$$2\ CH_3.CH. \longrightarrow CH_3.CH_3 + CH_2{:}CH_2$$

In none of these radical disproportionations, however, is the reaction mechanism properly understood.

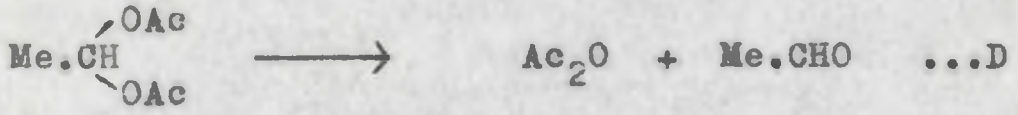
An analogous reaction is the disproportionation of esters on pyrolysis, whereupon the initial products may be an acid anhydride and an ether. This mechanism has been used by Hurd and Bennett (39) to explain the products of pyrolysis of benzyl benzoate, which, they state, include benzaldehyde, toluene, and benzoic anhydride:

$$2\ Ph.COO.CH_2Ph. \longrightarrow \begin{matrix} PhCO \\ PhCO \end{matrix}\!\!>\!O + \left[O\!<\!\begin{matrix} CH_2Ph \\ CH_2Ph \end{matrix} \right] \qquad \ldots D$$

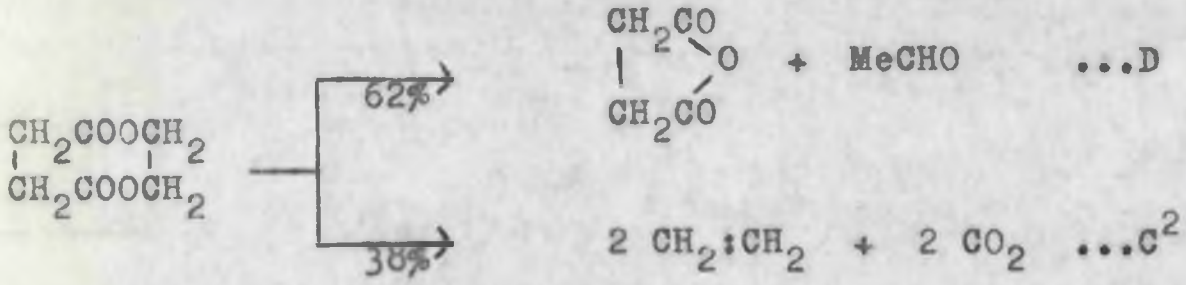
$$\downarrow$$

$$PhCHO + PhCH_3$$

This is supported by the knowledge that dibenzyl ether pyrolyses (40) to benzaldehyde and toluene. A direct result of this disproportionation is clearly the production of two molecules of greater symmetry than the original molecule. While it is obvious that two molecules of the pyrolysand are algebraically necessary for this reaction, the intermolecular mechanism involved (if such it is) is quite obscure, and certainly not simple. Similar reactions have been reported to occur in the esters of dihydric alcohols, and in this case it is somewhat easier to envisage the mechanism, as, for example, in the pyrolysis of ethylidene diacetate which has been reported by Geuther (41):

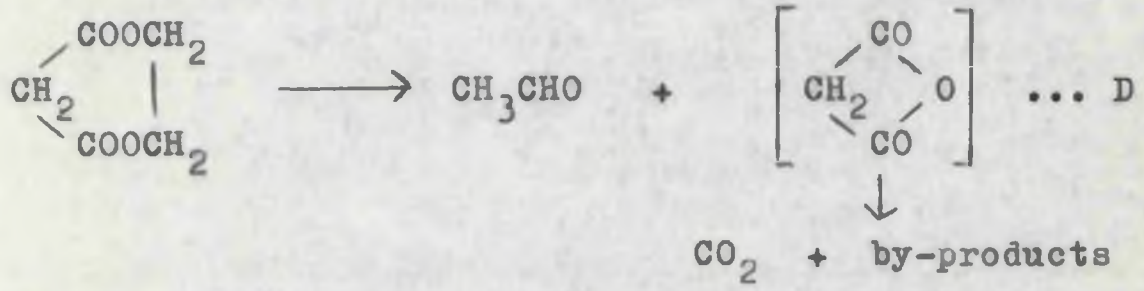


A somewhat different example is the pyrolysis of ethylene succinate, which is claimed by Tilicheev (42) to proceed by two routes:



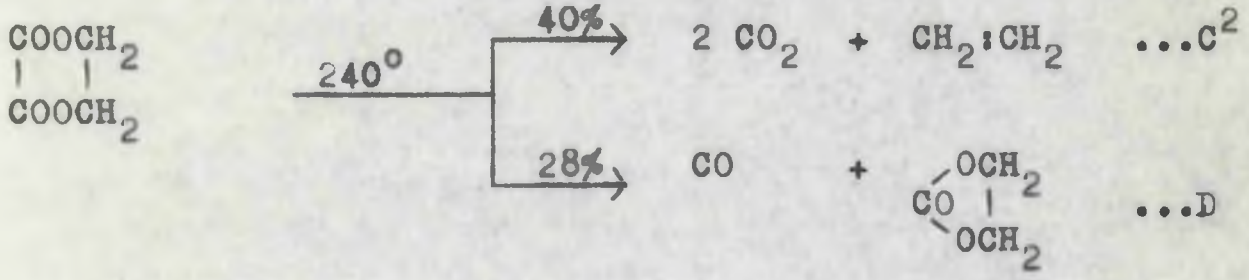
It seems likely that the main disproportionation produces succinic anhydride and ethylene oxide, which then rearranges to acetaldehyde. The existence of this reaction of ethylene oxide has been demonstrated by Peytral (43) and Mueller and Walters (44).

The pyrolysis of ethylene malonate (42) is much more complex, since a comparable disproportionation would yield malonic anhydride, which does not exist. However, it is claimed that there is evidence for the reaction:

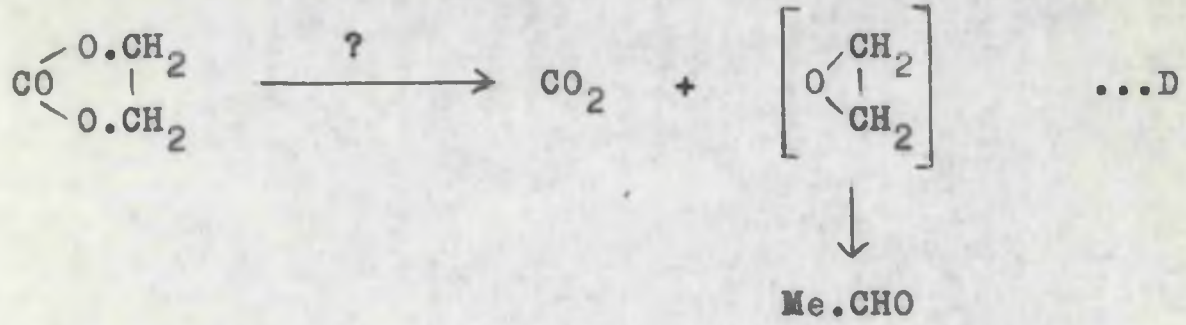


The other products of this reaction, ethylene diacetate and ethyl acetate may be the products of another disproportionation.

Tilicheev (45) has reported the pyrolysis of ethylene oxalate:



It seems reasonable to predict that under suitable conditions ethylene carbonate itself would disproportionate:



Another notable type of pyrolytic disproportionation may be

undergone by the mono-carboxylic esters of dihydric alcohols. Thus, Cretcher and Pittenger (46) have found that 2-hydroxyethyl benzoate disproportionates on distillation:

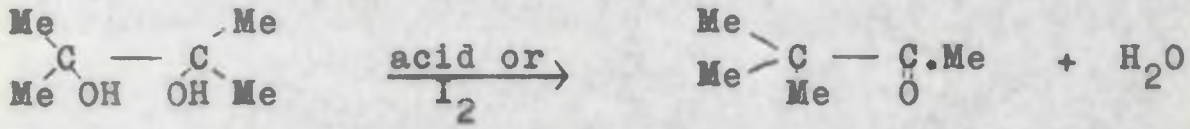
$$2\ BzO.CH_2.CH_2.OH \longrightarrow BzO.CH_2.CH_2.OBz + HO.CH_2.CH_2.OH \quad ...D$$

Again it is clear that this reaction has resulted in an increase in symmetry, which appears to be quite a general result of disproportionation reactions in the pyrolysis of esters.

1.1.6 : Molecular rearrangement, type R.

It is possible, by the judicious choice of examples, to show that throughout organic chemistry there is what has been called "the principle of minimum structural change". This principle requires that in any reaction the product will bear the closest possible relation to the main reactant (47). Hurd has shown the existence of a similar rule in the pyrolysis of organic compounds, which he has called the rule of "least molecular deformation", and Peytral (48) has quoted many examples in support of this. However, that this rule is not universally valid is very evident by the large number of molecular rearrangements which are known to occur, both thermally and by catalysis. A large proportion of these rearrangements may be classified as resulting from "1,2- shifts", which can be illustrated by the migration of the atom or group R from the atom A to the atom B:

A well known example of this type of rearrangement is the transformation of pinacol (tetramethylethylene glycol) into pinacolone (methyl tert.-butyl ketone) :



The mechanism of such a rearrangement has been considered by many workers, (inter al., Meerwein and v. Empstein, 49) and perhaps the most satisfactory explanation has been proposed by Whitmore (50), who has suggested that the loss of two electrons from the octet of atom B, forming an "open sextet" causes strain in the intermediate, which is therefore unstable,

and brings about the migration of the atom or radical R:

The strain which now exists in this second intermediate is relieved by combination with the radical :S, which has an unshared pair of electrons.

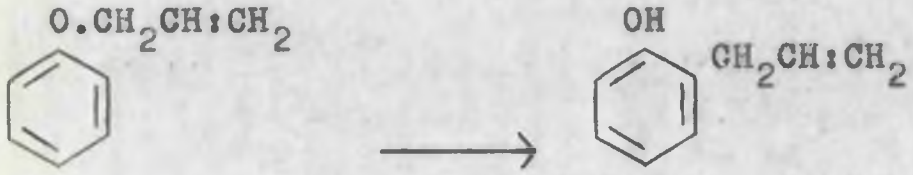
Another class of molecular rearrangement might be broadly

classified as the " 1,3- shift" type, although here it is not possible to generalise on the mechanism of the rearrangement. A good example is the Claisen Rearrangement (51) which occurs when the allyl ether of a phenol or an enol is heated to about 200°. Hurd and Pollack (52) have illustrated this reaction by the rearrangement of allyl vinyl ether into allylacetaldehyde:

$$CH_2{:}CHCH_2.O.CH{:}CH_2 \longrightarrow CH_2{:}CHCH_2CH_2.CHO$$

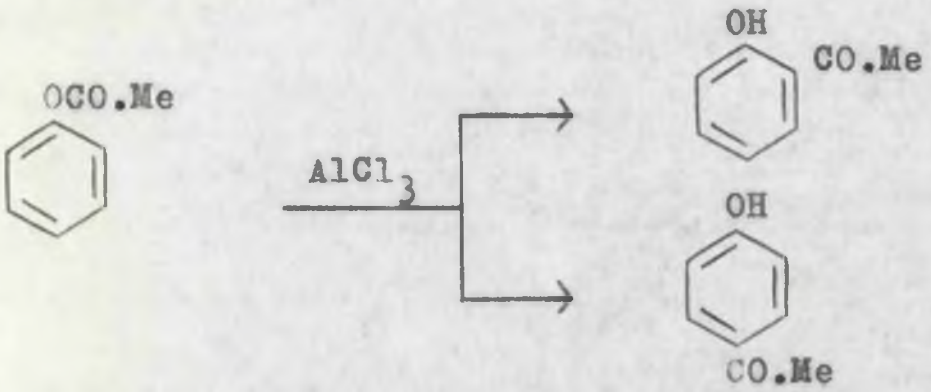
This gaseous conversion has been shown (53) to be a homogeneous gas reaction of the first order, which indicates that the rearrangement is intermolecular, and a reasonable mechanism would involve the redistribution of electrons and rearrangement probably <u>via</u> a cyclic intermediate:

Another example of this rearrangement is the transformation of allyl phenyl ether into <u>o</u>-allylphenol:



This last example bears a strong similarity to the Fries Rearrangement (54), which, however, occurs under the influence of a catalyst. Thus, the rearrangement of phenyl acetate

appears to follow a similar course:

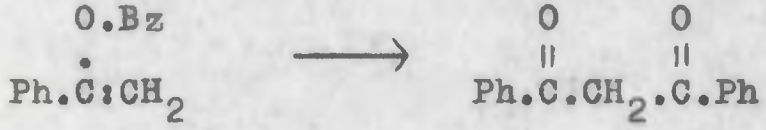


Recently, however, Hauser and Man (55) have studied this reaction, and, by means of interchange experiments, which yielded crossed products, they have concluded that the mechanism is intermolecular. It is interesting to note, by way of comparison, that when two Claisen Rearrangements are carried out together, (56), each behaves independantly of the other and no crossed products result. Hauser and Man have also considered the mechanism of the Fries Rearrangement, and they have postulated intermediate complexes involving the catalyst.

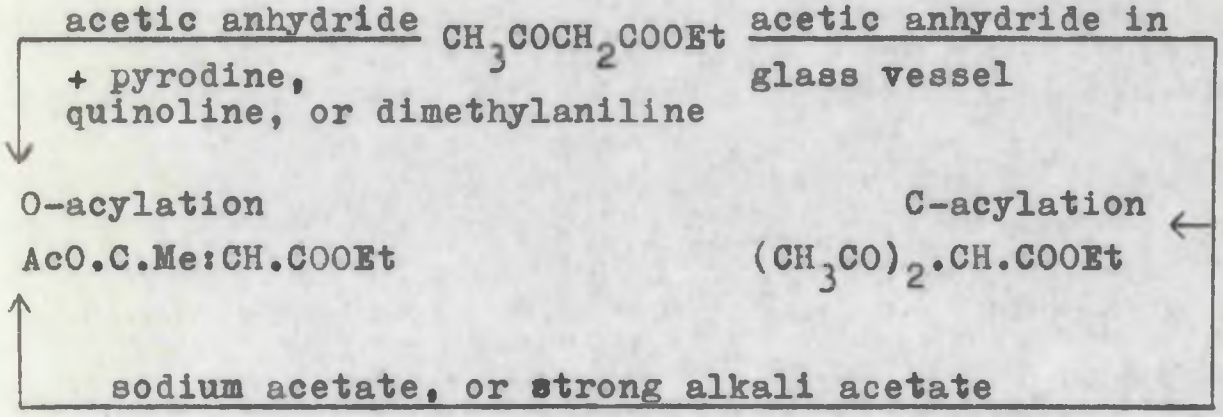
An example of the Claisen Rearrangement which is worthy of note is the transformation of ethyl O-allylacetoacetate (ethyl β-allyloxycrotonate) into ethyl α-allylacetoacetate, originally shown to occur in the presence of ammonium chloride (57), and later by purely thermal means (58):

This is an interesting example, because this type of migration

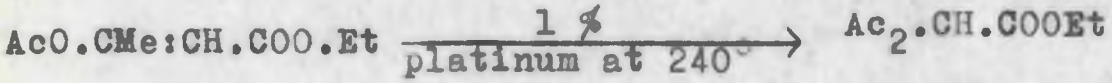
is also common to all O-acylacetoacetates, although, with the exception of the allyl ester, the reaction only occurs under the influence of bases. The catalysed rearrangement is known as the Claisen Transformation, and a similar rearrangement is found to occur with the esters of the enol form of ketones (59):



Another good example of this reaction has been shown by Dieckmann and Stein (60), who have shown that either O-acylation or C-acylation of acetoacetates can occur according to the chosen conditions, and that the O-acyl ester is converted to the C-acyl ester by the action of sodium acetate or strong alkali acetate:

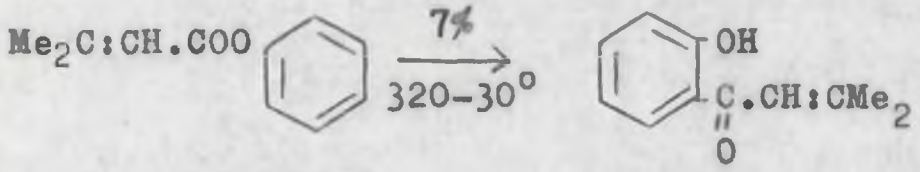


This work has been extended by Wislicenus (61), who found that the above rearrangements could take place thermally:



From a study of the literature it can be seen that, apart from the Claisen Rearrangements, there are very few reported

ester rearrangements which occur without the apparent aid of a catalyst. Skraup and Beng (34) have recorded that the aryl esters of β,β-dimethylacrylic acid rearrange to give an o-hydroxyketone:



A similar example has been shown by Skraup and Beifuss, (62) who heated phenyl cyclohexanecarboxylate in a sealed tube, and found cyclohexyl o-hydroxyphenyl ketone as a product of rearrangement:

Recently, it has been found by Boese and Young (63) that the esters of the enolic form of ketones rearrange thermally to yield β-diketones. It is claimed by these authors that this rearrangement is undergone by enol esters of the form,

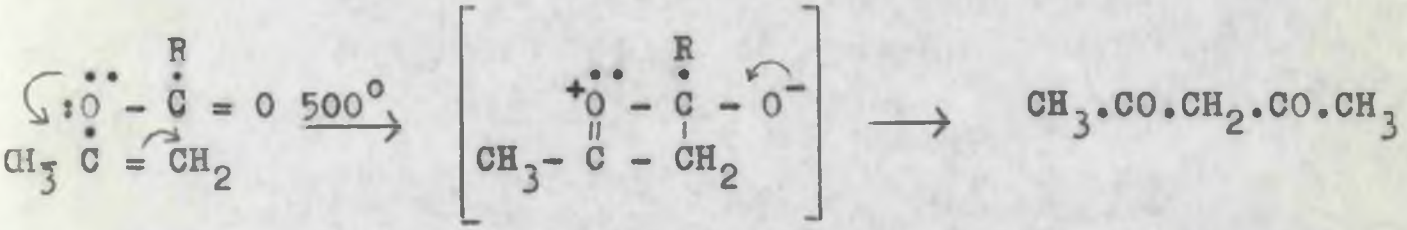
$$R_3.COO.CR_2{:}C <$$

where R_3 and R_2 may be aliphatic or aromatic radicals, or where R_2 together with the ethylenic carbon atoms may be part of an alicyclic ring. An example of this reaction is the

rearrangement of isopropenyl acetate into acetylacetone:

$$CH_3.\overset{\cdot}{C}(O.Ac):CH_2 \xrightarrow{500^\circ} Ac.CH_2COCH_3$$

This notable series of rearrangements has been the subject of further study by Young et al., (64) who have suggested that the reaction proceeds thermally by an intramolecular mechanism, involving a 4-membered cyclic transition stage. Thus, for example, the pyrolysis of isopropenyl acetate would be predicted to proceed in the following manner:



Young et al. have also shown that the same rearrangement may be effected at low temperature, using boron trifluoride as a catalyst, and for this they have postulated an intermolecular reaction mechanism, involving a complex addition compound as the intermediate.

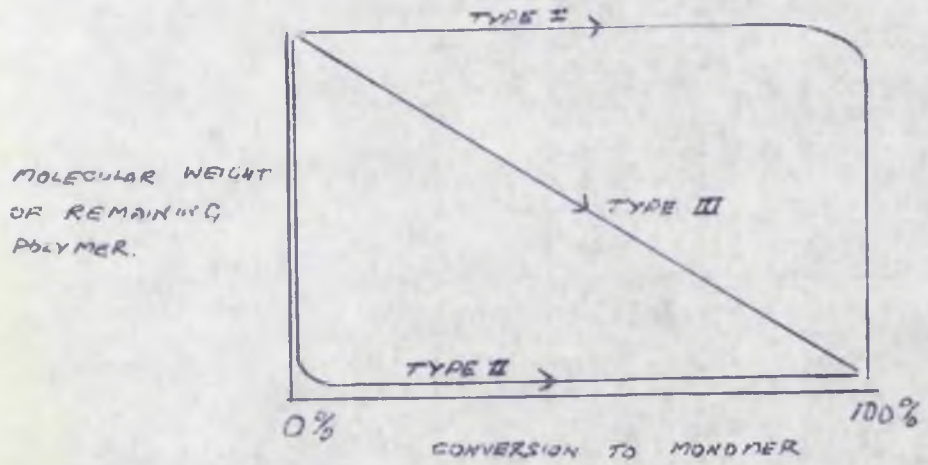
The Pyrolysis of Polymers and Polyesters.

1.2.1 : General.

The pyrolysis of pure polymers generally occurs at, and above, 300°, since at this temperature the thermal energy is sufficient to break the primary valence bonds between carbon atoms. This is true for pure polymers, but, where traces of residual catalyst or monomer are present, breakdown may take place by other means, for example, by chain transfer. The presence of weak links in polymers has been shown in several examples. Thus, in polyethylene the initial break occurs at the branches (Oakes and Richards, 65), and Grassie and Melville (66) have shown that the weak link in poly(methylmethacrylate) is actually at the chain end, and that consequently its susceptibility to rupture varies with the type of radical that initiated the chain, or the way in which it was terminated.

Wall (67) and Madorsky et al., (68) have investigated the pyrolysis of many polymers, and they have concluded that the ease of depolymerisation of the particular molecule depends on the conditions (a) that the polymeric radical is not stabilised by resonance nor suffers steric hindrance to reaction, (b) that the monomer so formed has extra resonance stability, and (c) that the polymer does not contain the easily removed tertiary carbon atoms. After the initial scission at the weakest link, the depolymerisation may then follow one of three courses of

degradation, and these have been represented by Melville (69) by the diagram below:

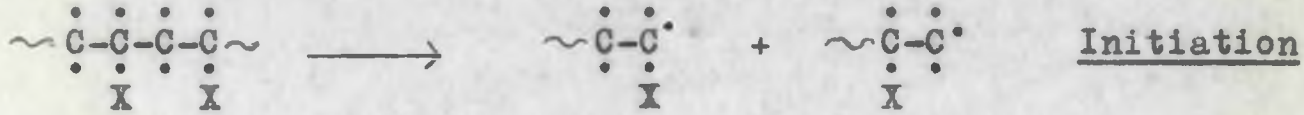


As an example of the first type (I), Grassie and Melville (66) have shown that in poly(methylmethacrylates) (of molecular weight about 50,000) the initial rupture is followed by complete depolymerisation of the polymer molecule, and this is fairly typical of vinyl polymers. Type II is in complete contrast, each chain-scission occurring in a completely random manner, which results in a large drop in molecular weight. This is regarded as the manner in which polyesters degrade, particularily those unable to form cyclic monomers, and also polyethylene. The third course is essentially a combination of I and II, and it is assumed that after the initial random scission, depolymerisation proceeds rapidly, but in one direction only. This last course is characteristic of certain vinyl polymers,

and also those polyesters and polyanhydrides which produce cyclic monomer at relatively low temperatures (Carothers and Spanagel, 70, also Carothers and Hill, 71). Generally speaking, polyesters which do not form cyclic monomers do not readily depolymerise to monomeric units, although poly(ethylene terephthalate), which can give a very small amount of cyclic trimer, (72) has been induced to degrade thus by the addition of glycol (73).

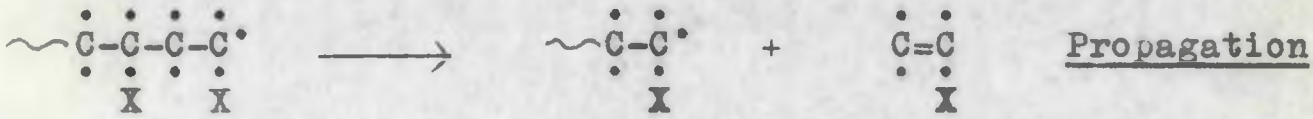
1.2.2 : Radical chain reactions in Polymer Pyrolysis.

In the degradation of vinyl-type polymers, it is possible to postulate a chain-reaction mechanism, similar in many respects to that postulated for the polymerisation of these compounds. This has been studied by Simha et al., (74, 75) who have suggested that the chain-reaction is initiated by random or terminal chain-scissions into radicals:



Initiation

The propagation step then involves the loss of monomer:



Propagation

It has been observed, however, that the vinyl polymers do not all degrade in the same manner and this has been explained by assuming chain transfer in the course of the reaction, either

by intermolecular or intramolecular transfer. Such a reaction is considered to be of importance in the degradation of polystyrene, and this is attributed to the presence of "vulnerable" tertiary hydrogen atoms. Thus chain transfer in this last case causes a rapid initial drop in molecular weight. In contrast, poly(methylmethacrylate) has no available tertiary hydrogen atoms, and hence degradation appears to affect only single polymer molecules, resulting in relatively little initial decrease in molecular weight.

The significance of tertiary hydrogen atoms has been illustrated by Grassie and Melville (66) by the incorporation of small amounts of acrylonitrile into the poly(methylmethacrylate) chain. The resulting copolymer then suffers rapid decrease in molecular weight in the initial stages of the pyrolysis. The above reactions are therefore interesting examples of the lability of tertiary hydrogen atoms, and clearly illustrate their ease of abstraction under these conditions. This is worthy of comparison with the behaviour of alkyl carboxylates on alkyl-oxygen siission (Type A) where the β-hydrogen atom is frequently abstracted from a primary carbon atom in preference to either a secondary or tertiary carbon atom.

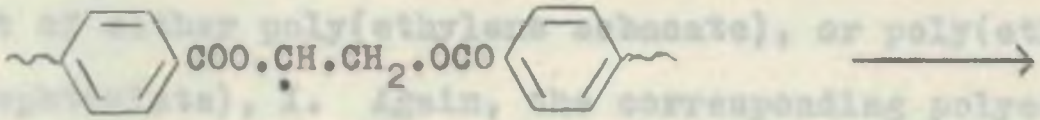
1.2.3 : Radical reactions in Polyester Pyrolysis.

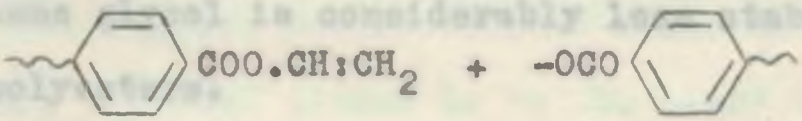
Very little investigation into the pyrolysis of polyesters has been reported, and, to date, what has been published has

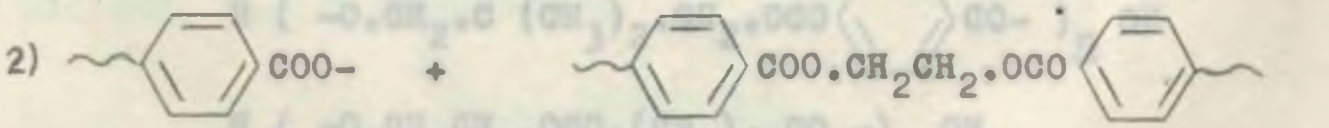
contained little information about the precise nature of the polyester decomposition. The pyrolysis of poly(ethylene terephthalate) ("Terylene") has been studied by Marshall and Todd (76), who have mainly restricted their examination to the kinetics of degradation by determinations of the melt-viscosity. From this, they have suggested that the polyester chains split in a random manner, probably at the ester group, and they have found evidence for the production of one carboxyl group per fission. They have concluded from their results that the reaction is one of essentially free radical character, and they have suggested suitable steps for the initiation and propagation of such a reaction. This is based on the assumption that the initiation step is the production of free radicals by a breakdown of unspecified (or, rather, unknown) nature, followed by an hydrogen atom transfer reaction:

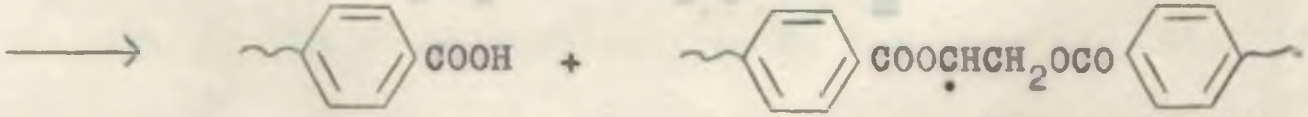
$$RH + R'. \longrightarrow R. + R'H$$

Thereafter, the following sequence of reactions could obtain:

1) 



2) 

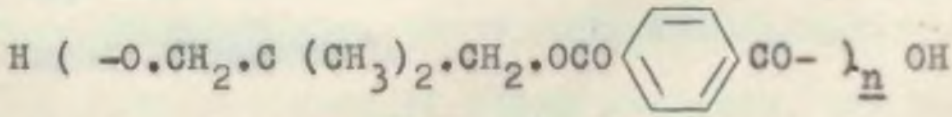


<u>Propagation</u>.

The above authors have followed this by further tentative chain reactions, but, in view of the very incomplete knowledge of the nature of the products of decomposition, it seems unwise to proceed any further in the pursuit of such highly hypothetical reactions.

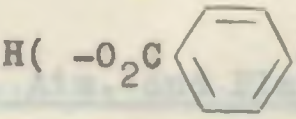
1.2.4: Relation of structure with thermal stability in polyesters.

The stability of several polyesters has been compared by Pohl (77), by the measurement of the rate of gas evolution, and the amount of colour change and acid formation. He has shown that polyesters are considerably less stable than polyethylene, and that this is presumably a result of the presence of the carboxyl group, -CO.O-. Furthermore, the presence of the methylene group in the position which is β to the ether oxygen atom also decreases the polyester thermal stability. Thus the thermal stability of the terephthalic polyester of 2,2-dimethylpropane-1,3-diol has been found to be considerably less than that of polyethylene, but greater than that of either poly(ethylene sebacate), or poly(ethylene terephthalate), I. Again, the corresponding polyester of diethylene glycol is considerably less stable than any of the above polyesters.



$$H\left(-O.CH_2.C(CH_3)_2.CH_2.OCO\langle\rangle CO- \right)_n OH$$

$$H\left(-O.CH_2CH_2.OCO.(CH_2)_8.CO- \right)_n OH$$



(I)

The Purpose, Aim, and Plan of this Work.

1.3.1 : Purpose and aim.

It has been shown in the preceeding section that, while several studies of polyester pyrolysis have been undertaken, few have considered fully or carefully enough the identification of the products. Thus a qualitative understanding of the nature of polyester thermal decomposition is lacking. It was therefore the purpose of this work to provide a basis for the investigation of the pyrolysis of linear polyesters, and in particular poly(ethylene terephthalate), and to discover the routes of thermal degradation. That such a study - if tackled directly by a study of the pyrolysis of the polyester itself - is overburdened by complexity, is clear from a study of the existing literature (e.g., 76, 77). Furthermore, an earlier attempt by this approach (Gilchrist and Ritchie, 78) confirmed the intractable nature of the problem.

Accordingly, since it was virtually unknown what happened to a polyester (or its fragments) after the initial split (presumed in the case of poly(ethylene terephthalate) to yield one carboxyl group per scission - Marshall and Todd, 76), a promising approach seemed to be the study of the pyrolysis of suitable "model compounds".

1.3.2 : The Plan : Model Compounds.

One of the chief difficulties in the interpretation of

polyester pyrolysis has been the inadequate knowledge of the behaviour of the ester group of aryl esters on pyrolysis. Because of this, it was extremely difficult to forecast how a polyester would decompose, and the inability to identify positively what products had resulted made it absolutely necessary to study simpler compounds, which contained the essential groupings of the polyester. For this reason model compounds were chosen, and these have been classified into five categories :

i) Specific segments, representing a unit, or part, of the whole polyester chain, and containing the same groupings and bonds.

ii) Terminal segments of the pyrolysed chain bearing new end-groups which might be predicted a priori.

iii) Transient segments, which might be predicted by virtue of the identification of the final products, but which cannot be isolated because of complete destruction.

iv) Homologous segments, containing slight structural modification to segments in classes (i) and (ii), chosen to demonstrate the relation between structure and thermal stability.

v) Intermediate segments, which have been identified as products of the decomposition of other segments, but which have been chosen for individual study to elucidate which products can be truly attributed to them.

The compounds chosen in these categories are shown in the table below :

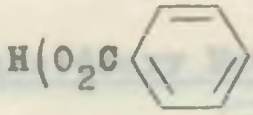
Compound.		Category.	Compound Number.
Ethylene dibenzoate	✱	i	II
Vinyl benzoate	✱	ii	III
Benzoylacetaldehyde		iii	IV
Ethylene		v	V
2-Benzoyloxyethyl terephthalate	✱	i	VII
4-Acetylbenzoic acid		iii	VIII
cycloHex-1-enyl benzoate	✱	iv	IX
2-Benzoylcyclohexanone		v	X
Acetylacetone		iv	XI
Trimethylene dibenzoate	✱	iv	XII
Allyl benzoate		v	XIII
Benzaldehyde		iii	XIV
Acrolein		v	XV
Propylene diacetate	✱	iv	XVI
Propylene dibenzoate	✱	iv	XVII
Allyl acetate		v	XVIII

(✱ = principal model compounds)

The reasons for the choice of II and IV are evident from the formula of poly(ethylene terephthalate), (I):

$Bz.O.CH_2CH_2.O.Bz$ (II)

$Bz.O.CH_2CH_2.OCO$  $COO.CH_2CH_2.O.Bz$ (IV)



(I) Bz.O.CH:CH_2 (III)

The choice of III rests upon the knowledge that, where an ester possesses a β-methylene group,

i) alkyl-oxygen scission, type A^1, will be the most likely mode of decomposition, yielding a carboxyl group and an unsaturated end-group (1), and,

ii) a point of weakness in polyesters appears to be at the β-methylene group (77) so confirming that a type A^1 scission would be expected.

Furthermore, Chitwood (79) has shown that the ester II pyrolyses to yield benzoic acid and III.

Of the principal model compounds,

(IX) Bz.O.CH_2.CH_2.CH_2.O.Bz (XII)

R.COO.CH_2.CHMe.OCO.R

(XVI : R = Me ; XVII : R = Ph)

IX has been chosen as a homologue of III (for reasons to be illustrated in the following section), and XII, XVI, and XVII have been selected to illustrate the influence of structure on the thermal decomposition of diesters, notably those where there has been a change in the central alkylene group and the relative availability of β-hydrogen atoms.

Following on the results of the above compounds, a number of other compounds have been chosen to explain further the results from these principal compounds.

Subsidiary Model Compound.		Related Principal Compound.
VIII	HOOC  CO.Me	VII
IV	$Bz.CH_2.CHO$	III
V	$CH_2:CH_2$	III
X		IX
XI	$Ac.CH_2.CO.Me$	IX
XIII	$CH_2:CH.CH_2.O.Bz$	XII
XIV	Ph.CHO	XII
XV	$CH_2:CH.CHO$	XII
XVIII	$CH_2:CH.CH_2.OAc$	XVI

The reasons for the inclusion of the above subsidiary model compounds within the general plan will be apparent in the following sections, since in all cases the choice was dependant upon the results obtained from the study of the principal model compounds.

The Pyrolysis of Model Compounds.

2 : General statement of results.

Ethylene dibenzoate decomposes by two routes, A^1 and D :

$$BzO.CH_2.CH_2.OBz \longrightarrow \begin{cases} BzOH + CH_2{:}CH.OBz & \ldots A^1 \\ \text{XIX} \quad\quad \text{III} & \\ Bz_2O + Me.CHO & \ldots D \\ \text{XX} \quad\quad \text{XXI} & \end{cases}$$

Route A^1 is clearly a straightforward example of this mode of scission, but, whereas route D was originally thought to be a pyrolytic reaction of II, it has now been found to be brought about by the reaction of XIX and III to yield ethylidene dibenzoate, VI :

$$\underset{\text{XIX}}{BzOH} + \underset{\text{III}}{CH_2{:}CH.OBz} \longrightarrow \left[\underset{\text{VI}}{Me.CH.(OBz)_2}\right] \xrightarrow{D} \underset{\text{XXI}}{Me.CHO} + \underset{\text{XX}}{Bz_2O}$$

This has been proved by the pyrolysis of XIX and III together, and also by further general study of this reaction.

The vinyl benzoate produced by the pyrolysis of ethylene dibenzoate was found to contain varying amounts of acetophenone, XXII, and this has been found to be the product of a type R reaction of III, followed immediately by a decarbonylation :

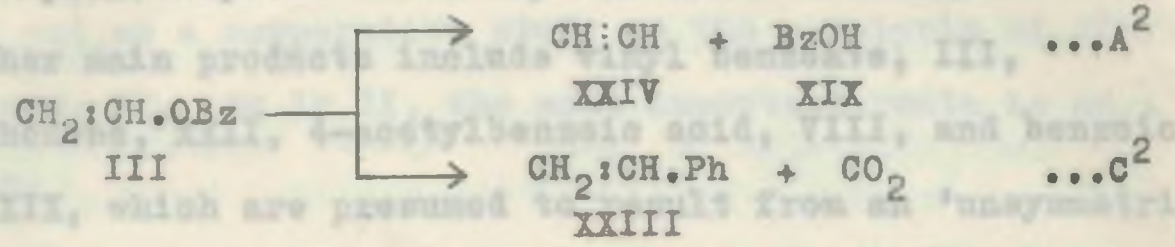
$$\underset{\text{III}}{CH_2{:}CH.OBz} \longrightarrow \left[\underset{\text{IV}}{Bz.CH_2.CHO}\right] \ldots R$$

$$\downarrow$$

$$Ph.CO.Me + CO \quad \ldots C^1$$

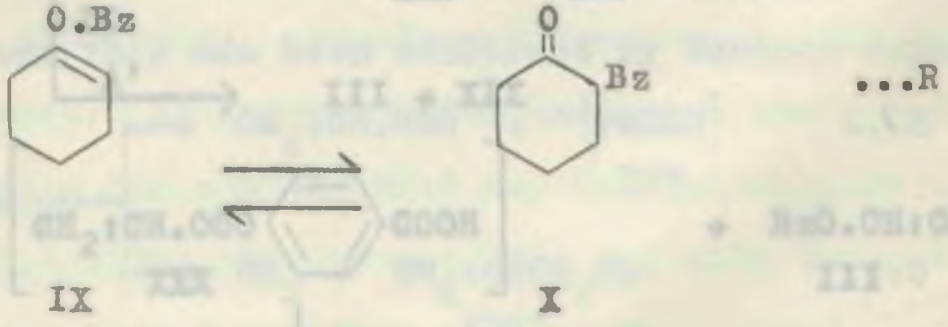
$$\text{XXII}$$

While it has been impossible to isolate IV as a product of pyrolysis of III (rearrangement), it has been found that IV does in fact yield XXII and carbon monoxide (decarbonylation). Two other competing routes have been found in the pyrolysis of III:



Both of these routes, however, are of less importance than the route R/C^1.

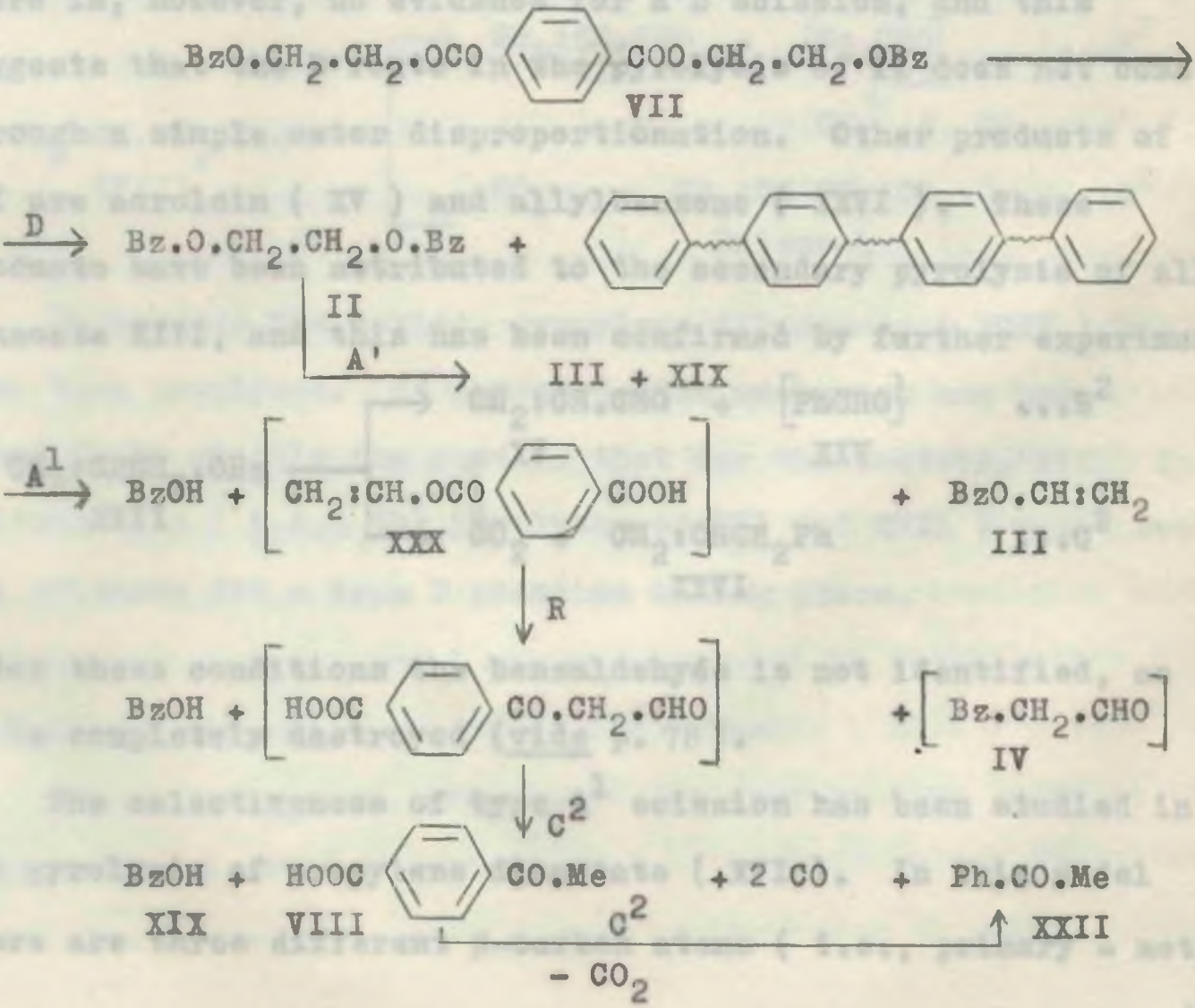
An analogous reaction to the rearrangement of III has been found to occur on the pyrolysis of cyclohex-1-enyl benzoate (IX), which rearranges to the stable β-diketone, 2-benzoylcyclohexanone (X). This reaction has been found to be reversible:



The pyrolysis of X has been compared with the pyrolysis of another diketone, acetylacetone (XI), which has been shown (63) to be the product of thermal rearrangement (type R) of isopropenyl acetate (XXXV), and evidence has now been found to suggest that this reaction also is reversible to a small extent:

XI XXXV

2-Benzoyloxyethyl terephthalate (VII) decomposes by route D to yield ethylene dibenzoate, II, and presumably a more complex compound which may contain four aromatic rings. The other main products include vinyl benzoate, III, acetophenone, XXII, 4-acetylbenzoic acid, VIII, and benzoic acid, XIX, which are presumed to result from an 'unsymmetrical' A^1 scission of VII. It should also be noted that III, XXII, and XIX could also be the A^1 products of II by route D.



The pyrolysis of VII, as in the pyrolysis of II, produces benzoic anhydride and acetaldehyde by a D reaction. This presumably is by the same mechanism that has been shown for the D route in II.

The pyrolysis of trimethylene dibenzoate (XII) has been carried out as a comparative study to the pyrolysis of ethylene dibenzoate, II. As in II, the most important route is an A^1 scission:

$$\underset{\text{XII}}{BzO.CH_2.CH_2.CH_2.OBz} \longrightarrow \underset{\text{XIX}}{BzOH} + \underset{\text{XIII}}{CH_2{:}CH.CH_2.OBz} \quad \ldots A^1$$

There is, however, no evidence for a D scission, and this suggests that the D route in the pyrolysis of II does not come through a simple ester disproportionation. Other products of XII are acrolein (XV) and allylbenzene (XXVI). These products have been attributed to the secondary pyrolysis of allyl benzoate XIII, and this has been confirmed by further experiment:

$$\underset{\text{XIII}}{CH_2{:}CHCH_2.OBz} \longrightarrow \begin{cases} \underset{\text{XV}}{CH_2{:}CH.CHO} + \underset{\text{XIV}}{[PhCHO]} & \ldots B^2 \\ CO_2 + \underset{\text{XXVI}}{CH_2{:}CHCH_2Ph} & \ldots C^2 \end{cases}$$

Under these conditions the benzaldehyde is not identified, as it is completely destroyed (vide p. 78).

The selectiveness of type A^1 scission has been studied in the pyrolysis of propylene diacetate (XVI). In this model there are three different β-carbon atoms (i.e., primary = methyl,

secondary = methylene, and tertiary = methylidyne) each bearing available β-hydrogen atoms, any of which, theoretically, could be involved in A^1 scission. It has been found, however, that, under the conditions of experiment, the β-hydrogen of the methyl (primary) group is taken preferentially and exclusively:

$$\underset{\text{XVI}}{AcO.CH_2.CHMe.OAc} \longrightarrow AcOH + \underset{\text{XVIII}}{CH_2{:}CH.CH_2.OAc} \quad \ldots A^1$$

Allyl acetate (XVIII) then pyrolyses in exactly the same manner as allyl benzoate

$$\underset{\text{XVIII}}{CH_2{:}CH.CH_2.OAc} \longrightarrow \begin{cases} \underset{\text{XV}}{CH_2{:}CH.CHO} + \underset{\text{XXI}}{[Me.CHO]} \rightarrow CH_4 + CO & \ldots B^2 \\ CO_2 + \underset{\text{Butene-1}}{CH_2{:}CH.CH_2.CH_3} & \ldots C^2 \end{cases}$$

To complete the series, propylene dibenzoate (XVII) has also been pyrolysed. As expected, the mechanism has been found to be exactly the same as that for the acetate, XVI. In neither case (i.e., the pyrolyses of XVI and XVII) was there any evidence for a type D reaction taking place.

The Pyrolysis of Model Compounds.

3 : Detailed statement and discussion of results.

3.1 : Ethylene dibenzoate (II), Vinyl Benzoate (III), and Benzoylacetaldehyde (IV).

3.1.1 : Vinyl ester rearrangements.

Although previous work (76-78) had explained very little about the fundamental nature of the qualitative mechanism of the pyrolysis of poly(ethylene terephthalate) (I), it was sufficiently clear from these studies that, in the light of the results of comparable pyrolyses, the behaviour of the polyester was anomalous. Thus, while Chitwood (79) had clearly shown that ethylene dibenzoate (II) cracked by an A^1 scission to yield vinyl benzoate (III) and benzoic acid, in none of the above polyester studies was there any indication of the presence of any vinyl-type end-groups such as would have been predicted. In order, therefore, to learn more about this apparent contradiction, the work of Chitwood was repeated, and a more intensive study of the pyrolysate was made. The results of this study were, in the main, in agreement with those of Chitwood, but the vinyl benzoate thus produced was found to contain a surprising amount of impurity, which could not be separated by distillation (80). This impurity was found to be acetophenone (XXII : b. 202°/760 mm.) which, in fact, has almost the same boiling point as vinyl benzoate (b. 203°/760 mm.), and it is quite clear therefore that these two substances cannot be separated by normal methods

of distillation. It was also clear that the quantities of acetophenone encountered were too large to have been produced by a minor route, and that this route was therefore a major mode of scission.

Another product, carbon monoxide, which had previously escaped detection, was found in large quantities, and, as in the case of acetophenone, it was by no means evident how this product could have been formed. It was, however, realised that these two rather surprising products, viz., acetophenone, XXII and carbon monoxide, corresponded to certain products found by earlier workers studying the pyrolysis of the polyester, I (78), viz., an unidentified carbonyl compound and carbon monoxide. Of the possible known sources of either, or both, of these new products, benzoic acid and ethylene dibenzoate both seemed much less likely than vinyl benzoate itself, although it was clear that vinyl benzoate could not yield them merely by a straight scission. However, it seemed reasonable to suggest that vinyl benzoate was the source, particularly since such a fission is feasible on a purely algebraic basis, i.e.,

$$\underset{\text{III}}{C_9H_8O_2} = \underset{\text{XXII}}{C_8H_8O} + CO$$

It therefore follows that if vinyl benzoate is the source of acetophenone and carbon monoxide, then some form of thermal rearrangement occurs as part of the reaction. By way of

finding a suitable postulate for the route of such a rearrangement, a study of the literature was made, and, although there are not many reported examples of purely thermal rearrangements, a very interesting analogy with the work of Boese and Young (63) was revealed. These authors have found that enol carboxylates undergo thermal rearrangement to yield β-diketones, and this, they have found, is true for a wide range of ketone enol carboxylates. This rearrangement has already been discussed, and examples shown, in an earlier section (1.1.6). Since vinyl esters may be considered as being the esters of the enolic form of acetaldehyde (i.e., the hypothetical vinyl alcohol), it seemed very likely that a similar mechanism might obtain here. Thus, while an enol carboxylate rearranges thermally to a β-diketone,

$$R_3.COO.CR_2{:}C\!<\ \xrightarrow{450^\circ}\ R_3.CO.\overset{|}{C}.CO.R_2 \qquad \ldots R$$

a vinyl ester would be predicted to rearrange to a β-ketoaldehyde:

$$R.COO.CH{:}CH_2 \longrightarrow R.CO.CH_2.CHO \qquad \ldots R$$

It is likely, however, that if such a rearrangement does occur, the β-ketoaldehyde will decompose further because of the relative instability of the aldehydic group, resulting in destruction (C^1).

It is therefore quite evident that the mechanism of Boese and Young can be applied, and used successfully to explain the

products of pyrolysis of vinyl benzoate:

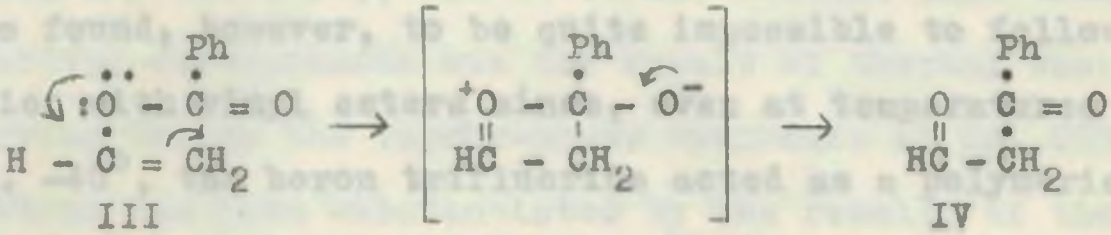
$$\underset{\text{III}}{\text{BzO.CH:CH}_2} \xrightarrow[\text{R}]{(1)} \underset{\text{IV}}{\text{Ph.CO.CH}_2\text{.CHO}} \xrightarrow[\text{C}^1]{(2)} \underset{\text{XXII}}{\text{Ph.CO.Me}} + \text{CO}$$

In order to test the validity of this theory, the pyrolysis of III and the ketoaldehyde, IV was carried out under the same conditions as hitherto used (i.e., in the pyrolysis of ethylene dibenzoate), and in each case, both acetophenone and carbon monoxide were identified as products in amounts comparable to those found in the pyrolysate from II. It has therefore been possible to furnish direct proof of the second stage (decarbonylation), but not however, of the first stage (rearrangement). The cause of this is considered to be the instability of benzoylacetaldehyde (IV), which precludes its isolation or identification. This is apparent from the study of the pyrolysis of IV, which decomposes completely at the temperatures generally used (i.e., ca. 500°), while at lower temperatures (i.e., ca. 400°) only a small amount survives. Furthermore, any attempt at distillation, even at low pressures (e.g., 1 mm. Hg) induces a large amount of resinification, with only about one third of the original compound surviving.

With reference to the decarbonylation of IV, it is of interest that Stahler (81) prepared the sodium enolate of IV by the reaction of acetophenone and carbon monoxide in the presence of sodium. This reaction, which was carried out at a very

high pressure over a lengthy period, is virtually the reversal of the pyrolytic decarbonylation shown above.

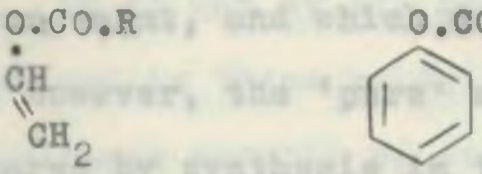
It seems fairly convincing, therefore, that rearrangement to the ketoaldehyde is the primary stage of the reaction, particularily since vinyl benzoate has been found to yield the same products as the ketoaldehyde itself. The actual mechanism of the thermal rearrangement of the enol carboxylates has been considered by Young et al. (64), and they have proposed that the reaction is intramolecular, with the formation of a four-membered transient cyclic state (cf. section 1.1.6). This interpretation can be satisfactorily applied to the case of vinyl benzoate:



III IV

The relationship between rearrangements of purely thermal character (cf. section 1.1.6), and those brought out under the influence of catalysts is of considerable importance, because it is sometimes found that both types can be observed for the same compound. Thus the base-catalysed rearrangements described by Dieckmann and Stein (60) have also been shown by Wislicenus to occur by purely thermal means. Again, the rearrangement of enol carboxylates has been shown to occur (61) by an intramolecular thermal reaction, and under the influence of boron

trifluoride by an intermolecular reaction. Because of this, therefore, it seemed of value to determine whether vinyl benzoate also could be induced to rearrange under the influence of a suitable catalyst. Clearly, if it was found that this occurred, there would be a strong similarity between the rearrangement of vinyl benzoate and the Fries Rearrangement (cf. section 1.1.6) of certain esters, e.g., phenyl carboxylate:



vinyl benzoate (R = Ph) phenyl carboxylate

It was found, however, to be quite impossible to follow this reaction with vinyl esters since, even at temperatures as low as ca. -40°, the boron trifluoride acted as a polymerisation catalyst with explosive violence. Furthermore, the use of boron trifluoride etherate, in an attempt to mitigate this effect, was equally unsuccessful. This property of boron trifluoride is, however, not surprising, in view of its known properties as a polymerisation catalyst, (e.g., for isobutylene at - 80°).

3.1.2 : Extent of vinyl ester rearrangement.

The investigations, detailed above, which have shown and explained the vinyl benzoate rearrangement, were carried out within the temperature range 500-550°. In order, therefore,

to extend this study to a fuller temperature range and thereby discover what effect lower temperature had on the rearrangement, a series of studies of the pyrolysis of vinyl benzoate was carried out within the temperature range 300-550°.

This investigation revealed that, at all the temperatures within this range, there had been produced a substantial amount of acetophenone which had definitely arisen from the thermal rearrangement, and which decreased with the temperature. In all cases, however, the 'pure' starting material (vinyl benzoate prepared by synthesis in the vapour-phase) already contained varying amounts of acetophenone (actually, values between 1 % and 7 %), and it became evident that this 'impurity' acetophenone was the result of thermal rearrangement occurring during the vapour-phase synthesis at ca. 250°. This deduction has been substantiated by the results of the study of the pyrolysis of vinyl benzoate over the extended temperature range. This showed that when the acetophenone content (A) of the pyrolysate (i.e., that amount of acetophenone which had actually been produced in the course of pyrolysis) is plotted against the temperature (T = 300-550°), the relationship is almost linear. In point of fact, this relationship is only approximate because of the existing experimental variations, but, with this in mind, it seems quite permissable to represent the results by the equation:

$$T = 14.2\,A + 190$$

The constant (190) of this equation is particularily interesting, because this can be interpreted as the " threshold " temperature, above which the rearrangement occurs and acetophenone is produced. Since, however, it is actually lower than the boiling point of vinyl benzoate (b. 203°/ 760 mm.) it appears that any vinyl benzoate handled at, or above, its boiling point will not be rigorously pure, but will contain some amount of acetophenone. It is not at all surprising, therefore, that the vinyl benzoate used in these experiments should have contained such relatively large amounts of acetophenone (up to 7 %) since the temperature of synthesis was ca. 250°. Furthermore, it is now possible to understand why the literature has such a paucity of physical data for vinyl benzoate, since it is most probable that all the earlier methods of synthesis involved high temperatures and hence led to an impure product.

It has been pointed out above that Chitwood did not report any impurity in the vinyl benzoate produced by him. It is possible, however, that the quantities involved were of a much smaller order, because of the different experimental technique employed. Thus, all the vinyl benzoate was removed through a still-head (maintained at 220-240°) immediately it was formed (from a reactor maintained at 360-425°), and so, for the vinyl benzoate, only a very short contact-time was involved. In contrast, however, the polyester studies (76 - 78) all involved very large contact-times, and as a result it appears that any vinyl

ester produced may have suffered destruction through a similar thermal rearrangement. This aspect, however, will be considered in a later section (4.1).

3.1.3 : The behaviour of vinyl esters in pyrolytic disproportionation reactions.

The second route of importance in the pyrolysis of ethylene dibenzoate is that which produces benzoic anhydride (XX) and acetaldehyde (XXI). It has been found that XX is produced from neither vinyl benzoate nor benzoylacetaldehyde on pyrolysis, and that benzoic acid itself (section 7.6.2) only gives XX in very small amounts, which are quite insufficient to explain its presence above. It was therefore originally considered that these products were formed by a type D reaction of ethylene dibenzoate. Thus, a reaction after the general scheme shown below was envisaged,

$$\underset{\text{II}}{BzO\,CH_2.CH_2.O\,Bz} \longrightarrow \underset{\text{XX}}{Bz_2O} + \underset{\text{XXI}}{Me.CHO} \quad \ldots D$$

although the precise mechanism of such a reaction is rather obscure. However, there appeared reason to question the above route, and accordingly, a series of investigations into this type of reaction was carried out.

This investigation was based on the knowledge that a carboxylic acid will add across the double bond of the corresponding vinyl carboxylate to yield an ethylidene diester, thus:

$$R.COOH + CH_2{:}CH.OCO.R \longrightarrow CH_3.CH(OCO.R)_2$$

(in the presence of a catalyst)

This reaction has been reported where R = Me (82) and R = Ph (83), and also, using suitable amounts, it has been shown that it is possible to prepare both the diacetate and vinyl acetate from acetylene and acetic acid (84):

$$AcOH + CH{:}CH \xrightarrow{HgO} \begin{cases} Me.CH(OAc)_2 \\ CH_2{:}CH.OAc \quad (25\ \%) \end{cases}$$

It is obvious, therefore, that vinyl acetate is in fact an intermediate in this reaction, and not a by-product as suggested. To discover whether a similar reaction occurred on pyrolysis, therefore, equimolar quantities of benzoic acid and vinyl benzoate were copyrolysed under the standard conditions, and it was found that there was formed a substantial amount of benzoic anhydride, XX, and acetaldehyde, XXI. This important result clearly suggested that the above reactions obtained and that the intermediate in the pyrolytic formation of XX and XXI was ethylidene dibenzoate (VI). That VI should so pyrolyse is not surprising, since it has been shown that ethylidene diacetate behaves in exactly the same manner (41), and, as the result of further work, it now appears that this is the general route for this type of reaction. That this is the case has been shown by the following:

i) equimolar quantities of vinyl benzoate and benzoic acid have been found to react at 260-300° in the absence of any catalyst, to yield almost quantitatively XX and XXI, and

ii) equimolar quantities of vinyl acetate and acetic acid have been found to react with a mercury catalyst to yield ethylidene diacetate (although this reaction does not appear to take place without a catalyst).

Hence, it appears to be reasonably certain that the D route of the pyrolysis of ethylene dibenzoate involves the products of the A^1 route which then react to give the intermediate VI which immediately breaks down to XX and XXI:

$$BzO.CH_2.CH_2.OBz \longrightarrow BzOH + BzO.CH{:}CH_2 \quad \ldots A^1$$

$$\longrightarrow \left[(BzO)_2CH.CH_3\right] \quad (VI)$$

$$\longrightarrow \underset{XX}{Bz_2O} + \underset{XXI}{Me.CHO} \quad \ldots D$$

3.1.4 : The decarboxylation of vinyl benzoate.

The examination of the infrared spectra of all the fractions and intermediate fractions of the pyrolysate of vinyl benzoate revealed that the intermediate fraction with the boiling range just below vinyl benzoate, contained some hitherto undiscovered substance. This was readily identified as styrene, which was present in quantites probably not exceeding 2-3 %.

There are two possible ways in which this product could be formed; firstly, by simple decarboxylation (C^2) of vinyl

benzoate and, secondly, by the reaction of two other products, benzene and acetylene:

1) $Ph.COO.CH{:}CH_2$ (III) $\longrightarrow$ $Ph.CH{:}CH_2$ (XXIII) + CO_2 ...C^2

2) C_6H_6 + $CH{:}CH$ (XXIV) $\longrightarrow$ $Ph.CH{:}CH_2$ (XXIII)

In view of certain evidence (85) on the chemistry of acetylene, however, the second route seems rather unlikely, and so the route by decarboxylation is the one favoured.

This result is of great interest because, as mentioned above, (section 1.1.4) there are very few examples of ester decarboxylation. This, of course, may have been caused by the reaction being of relatively minor extent and importance compared with the main reaction, and thereby escaping notice.

The mechanism of C^2 reactions is still quite obscure, but it is noteworthy that so many of the known examples - together with this new one - should contain an unsaturated group adjacent to the ester linkage, and it may well be that this fact has some bearing on the ability of an ester to decarboxylate.

3.1.5 : Other routes in the pyrolysis of vinyl benzoate.
(a) Alkenyl-oxygen scission (A^2).

This route is present to only a small extent (8 % at 500^o), and is quite a minor route compared to the R/C^1 route. It is possible that the ethenoid double bond causes strain in the six-membered intermediate proposed by Hurd and Blunck (5),

so reducing the extent of this route in favour of the R/C^1 reaction.

(b) Acyl-oxygen scission (B).

Of the two possible routes of this type of scission (B^2 and B^1), only B^1 could obtain in the case of vinyl benzoate, since there is no available α-hydrogen atom on the phenyl group (necessary for B^2 scission):

$$Ph.COO.CH{:}CH_2 \xrightarrow{?} Ph.CHO + CH_2{:}CO \quad \ldots B^1$$

In no cases, however, was there any trace of either keten or benzaldehyde, although the latter could have been pyrolysed further. A careful search was made for keten, but since none was detected, it was concluded that this product was therefore absent.

Further studies (86) have shown that vinyl esters which crack by a B route, actually do so by the B^2, and not the B^1, route. Since vinyl benzoate is structurally precluded from a B^2 route, it can therefore be appreciated why it does not crack by any acyl-oxygen route.

3.1.6 : Other products isolated in the pyrolysis of vinyl benzoate

(a) Benzene.

This is the product of straight decarboxylation of benzoic acid, which is, of course, a well-known reaction: Taken together with the decarboxylation of vinyl benzoate (C^2), these two routes together explain the relatively high proportion of carbon

dioxide observed.

(b) Methane.

This product has been identified mainly by infrared analysis, and is not present in any appreciable amounts. It is most likely to be the product of decomposition of acetaldehyde, itself present in only small quantities.

(c) Ethylene.

This product has also been identified by infrared analysis, and appears to constitute a considerable amount of the total unsaturated hydrocarbons analysed. At the present, however, there is no obvious route which would produce this gas, and its origin therefore remains obscure.

(d) Unknown gas.

In addition to the other known gases, the infrared spectrum has repeatedly shown the presence of an unknown gas (absorption, 1140 cm^{-1}, sharp.) which has not been identified.

3.1.7 : The pyrolysis of vinyl benzoate over stainless steel.

A quantity of vinyl benzoate was pyrolysed in the standard manner, with the exception that the reactor was packed with fresh turnings of stainless steel in place of the usual glass packing. By this means it was possible to discover whether any further cracking would take place because of the influence of the stainless steel.

While no difference in the solid and liquid pyrolysate

could be found, there was a clear change in the gas pyrolysate. In contrast to previous runs, the gas analysis showed considerable amounts of hydrogen and paraffin gases, while the amount of unsaturated hydrocarbon gases had dropped very considerably.

There are several sources from which this hydrogen might arise, but it seems very likely that its presence is inter-related to the diminution in quantity of unsaturated hydrocarbons. To settle this point, therefore, pure ethylene gas was pyrolysed under identical conditions, and it was found that this yielded hydrogen and paraffin gases in almost the same molar ratio as in the corresponding pyrolysis of vinyl benzoate. This, therefore, appears to be the only effect caused by the stainless steel which differs from the 'uncatalysed' pyrolyses.

3.2 : 2-Benzoyloxyethyl terephthalate (VII) and 4-Acetylbenzoic acid (VIII).

3.2.1 : 2-Benzoyloxyethyl terephthalate; the possible complexity of results.

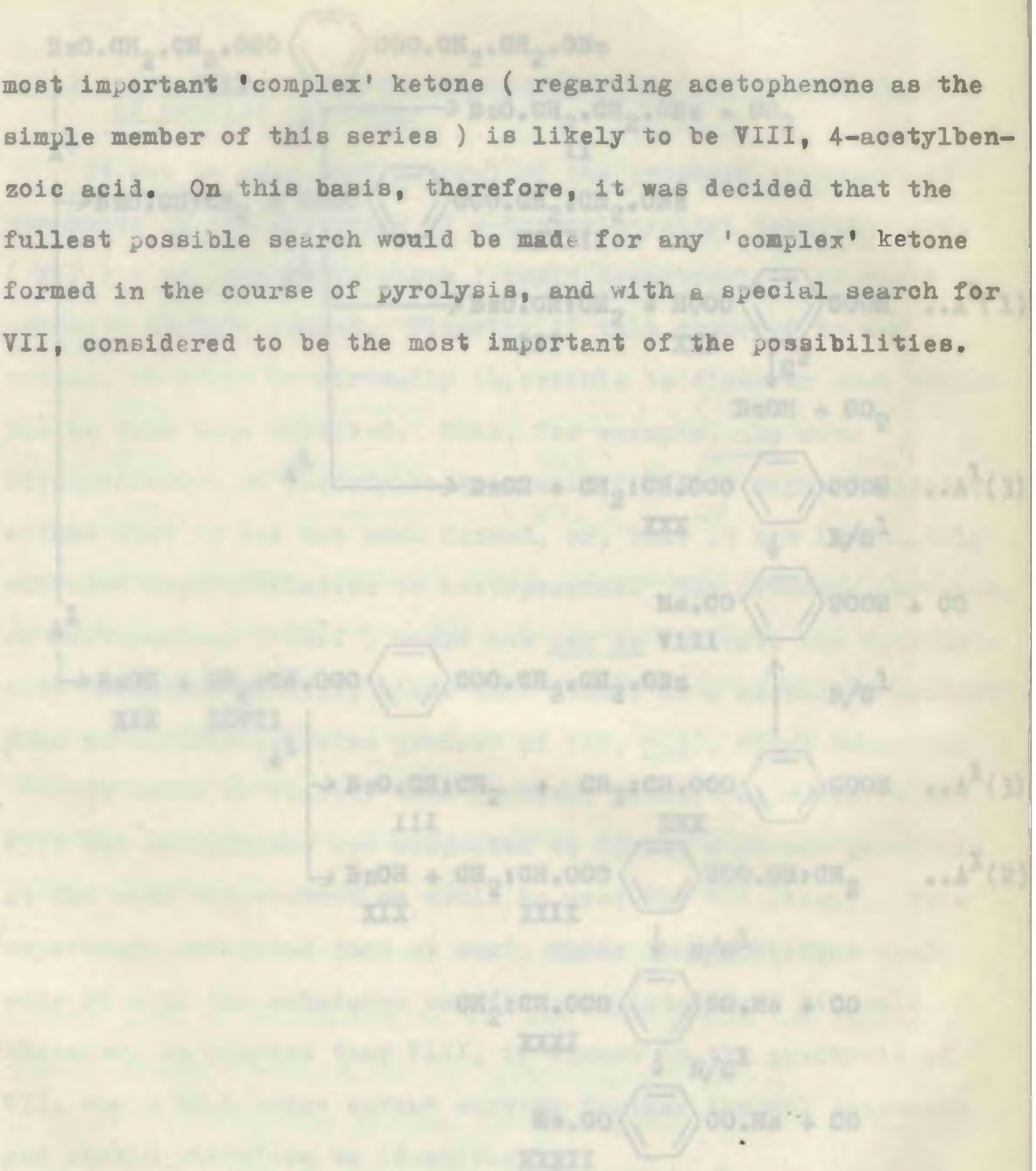
As a result of the study of ethylene dibenzoate (II), the first model compound in category (i), it has been shown that the vinyl ester produced by the A^1 scission of II does not wholly survive pyrolysis, but is partly decomposed itself by a thermal rearrangement (R/C^1 route). While this result is itself of great importance, it cannot, however, be directly used as a point of comparison with the polyester itself, since the frag-

ments of the polyester will most certainly be esters or compounds related to terephthalic acid rather than benzoic acid. It would, therefore, be unwise to assume that a mono- or divinyl terephthalate will rearrange in the same manner as vinyl benzoate.

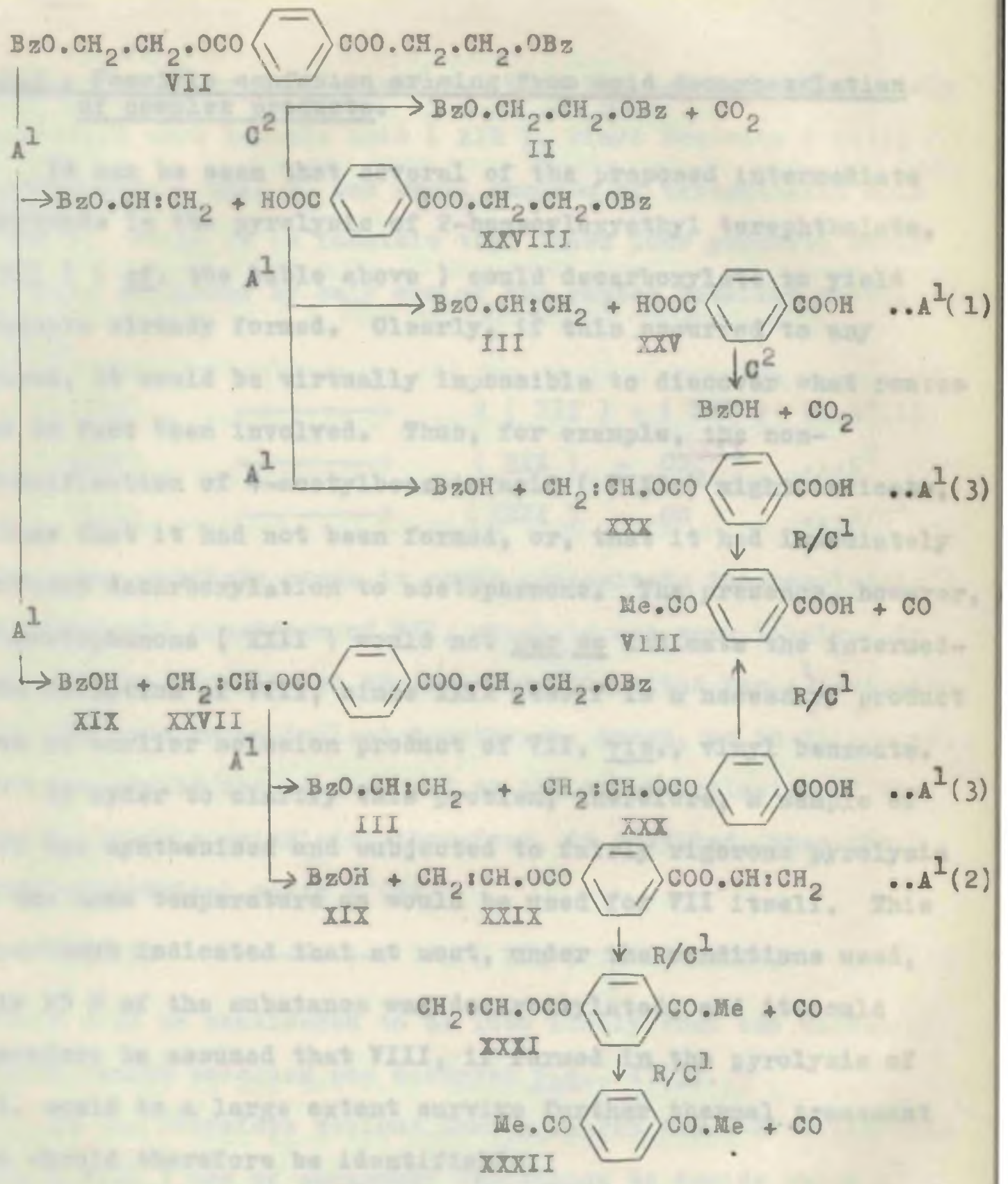
The second model compound of this first category, therefore, which has been chosen, possesses the same alkylene group and ester linkages as II, but, in this case, by virtue of having three aromatic rings, its 'nucleus' is a terephthalic ester, which, like the polyester I, is perfectly symmetrical. This ester, 2-benzoyloxyethyl terephthalate (VII), can in theory undergo a type A^1 scission in several different ways, and if, at this stage, it is assumed that all vinyl esters so-formed are capable of rearrangement (route R/C^1, as that undergone by vinyl benzoate) then it is evident that VII could yield several carbonyl compounds. Such a scheme is shown in the table below, in which every possible A^1 scission is followed, and also all the possible R/C^1 products which could theoretically be produced.

It can be seen from this table that, where scission has occurred at both sides of the terephthalic unit, then either the same two fragments are formed (i.e., two molecules of either vinyl benzoate, III, or benzoic acid, XIX) or, III comes from one side, and XIX from the other, leaving the 'unsymmetrical' residue, vinyl hydrogen terephthalate, XXX. Since scission is most likely to occur in a random manner, then it is probable that the last route will be the predominant one, and hence the

most important 'complex' ketone (regarding acetophenone as the simple member of this series) is likely to be VIII, 4-acetylbenzoic acid. On this basis, therefore, it was decided that the fullest possible search would be made for any 'complex' ketone formed in the course of pyrolysis, and with a special search for VII, considered to be the most important of the possibilities.



The possible end-products of an initial A^1 scission of 2-benzoyloxyethyl terephthalate.



The possible end-products of an initial A^1 scission of 2-benzoyloxyethyl terephthalate.

3.2.2 : Possible confusion arising from acid decarboxylation of complex products.

It can be seen that several of the proposed intermediate compounds in the pyrolysis of 2-benzoyloxyethyl terephthalate, (VII) (cf. the table above) could decarboxylate to yield products already formed. Clearly, if this occurred to any extent, it would be virtually impossible to discover what routes had in fact been involved. Thus, for example, the non-identification of 4-acetylbenzoic acid (VIII) might indicate, either that it had not been formed, or, that it had immediately suffered decarboxylation to acetophenone. The presence, however, of acetophenone (XXII) would not per se indicate the intermediate formation of VIII, since XXII itself is a necessary product from an earlier scission product of VII, viz., vinyl benzoate.

In order to clarify this problem, therefore, a sample of VIII was synthesised and subjected to fairly rigorous pyrolysis at the same temperature as would be used for VII itself. This experiment indicated that at most, under the conditions used, only 25 % of the substance was decarboxylated, and it could therefore be assumed that VIII, if formed in the pyrolysis of VII, would to a large extent survive further thermal treatment and should therefore be identifiable.

3.2.3 : The pyrolysis of 2-benzoyloxyethyl terephthalate (VII).

The initial examination of the pyrolysate of VII indicated, as expected, that by far the greatest amount of breakdown had

occurred by A^1 type of scission. Thus the products immediately identified were benzoic acid (XIX), vinyl benzoate (III), acetophenone (XXII), and small amounts of terephthalic acid (XXV). While it is feasible that these four products could be fully explained by only one of the routes detailed above, $A^1(1)$:

$$(VII) \longrightarrow 2\,(III) + (XXV) \quad \ldots A^1(1)$$

$$(XXV) \longrightarrow (XIX) + CO_2 \quad \ldots C^2$$

$$(III) \longrightarrow (XXII) + CO \quad \ldots R/C^1$$

this seems unlikely since it would necessitate the completely 'symmetrical' breakdown of VII, which is not very likely. In other words, where there are two possible sites for A^1 scission, and both have an equivalent β-methylene group, as in this case, then one should not be favoured to the total exclusion of the other. If this principle, therefore, is accepted, then the other symmetrical route $A^1(2)$,

$$(VII) \longrightarrow 2\,(XIX) + (XXIX)$$

should also be considered to be less likely than one where purely random scission has occurred i.e., $A^1(3)$.

It was therefore obvious that a search for 4-acetylbenzoic acid (VIII) was of paramount importance to decide which A^1 route was the most important. This was fraught with greater difficulties than had at first been realised, and attempts to isolate suitable derivatives of VIII invariably failed, yielding

only the derivative of acetophenone itself. To overcome this difficulty, therefore, paper chromatography has been employed (87), and has been very successful in providing this identification.

Using this technique, it has been possible to identify 4-acetylbenzoic acid (VIII), positively identified as its 2:4-dinitrophenylhydrazone, and the results have shown that it is present in quantities a little smaller than those of the derivative of acetophenone itself. This result is of great significance because, (a) it shows that route $A^1(3)$ is probably the major route of pyrolysis, and (b) since it is most unlikely that VIII could have resulted from any other source but the R/C^1 route from XXX (vinyl hydrogen terephthalate), it shows that a vinyl terephthalic ester is capable of the vinyl benzoate type of rearrangement.

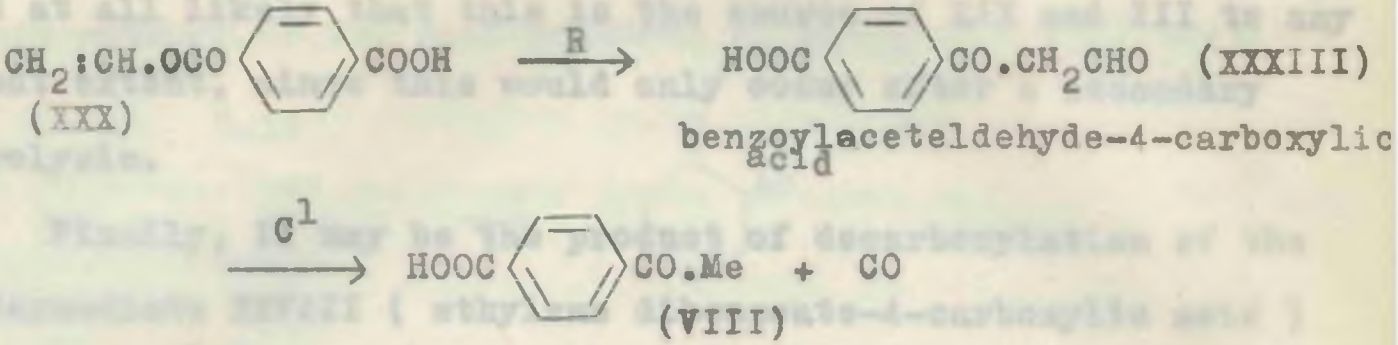
The main mode of A^1 scission of VII may therefore be represented thus,

$$(VII) \longrightarrow (III) + (XXX) + (XIX) \quad \ldots A^1(3)$$

$$(XXX) \downarrow$$

$$(VIII) + CO \quad \ldots R/C^1$$

and, although it has not been possible to identify XXX in this present work, this does not mean that its presence, already inferred, should not be capable of proof. If, as may be expected, the mechanism of the R/C^1 route of XXX is the same as that suggested for vinyl benzoate,



then it is most unlikely that any evidence of XXXIII could be found, and again it would probably follow that any other theory to explain these products would be quite untenable in the light of the experimental evidence.

Another product, which is probably linked with those, is benzene. This has been found in small quantities, and is most certainly the product of decarboxylation of benzoic acid.

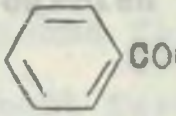
3.2.4 : Disproportionation in the pyrolysis of 2-benzoyloxyethyl terephthalate (VII).

Three products have been found, benzoic anhydride (XX), acetaldehyde (XXI), and ethylene dibenzoate (II), all of which may be attributed to disproportionation. Of these, XX and XXI are most probably formed by the same mechanism as proposed for their formation in the pyrolysis of II, viz., the reaction of benzoic acid and vinyl benzoate to form ethylidene dibenzoate, which then cracks to give XX and XXI.

In this pyrolysis both benzoic acid (XIX) and vinyl benzoate (III) have been produced in fair quantity, by the direct scission of VII, and although II is also present, it is

not at all likely that this is the source of XIX and III to any great extent, since this would only occur after a secondary pyrolysis.

Finally, II may be the product of decarboxylation of the intermediate XXVIII (ethylene dibenzoate-4-carboxylic acid) in routes $A^1(1)$ and $A^1(3)$, or it may arise from a genuine disproportionation of VII. If the latter is the case, then there should be some other, and larger, fragment. Such a mechanism might produce a ' four-ring ' compound:

2 (VII) → (II) + BzO.CH_2CH_2.(OCO  COO.CH_2CH_2)$_2$.OBz

...D

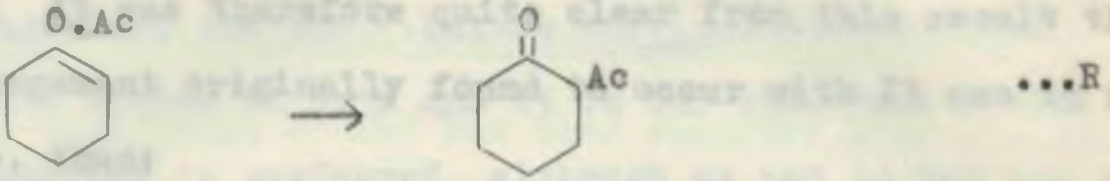
As yet there is no evidence to support this directly, but it is quite possible, particularily as the polyester (I) has been found to yield a cyclic trimer (72) on pyrolysis, and this is presumably formed by a similar mechanism. At the moment, however, the former route must be regarded as equally likely, since there is very definite evidence that such a route occurs.

3.3 : cyclo**H**ex-1-enyl benzoate (IX) and 2-benzoylcyclohexanone (X).

3.3.1 : The thermal rearrangement of cyclohex-1-enyl benzoate.

The study of the pyrolysis of vinyl benzoate has revealed the similarity between the rearrangement undergone by this ester, and the rearrangements of the enol carboxylates as reported by Boese and Young (63). Amongst the many examples quoted by

these authors is the rearrangement of cyclohex-1-enyl acetate:

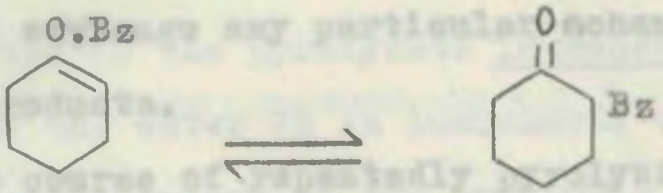


There is, however, no mention of the aromatic analogue, cyclohex-1-enyl benzoate (IX), and so it was decided that a full study of this compound would make an interesting and valuable parallel to the study already carried out on vinyl benzoate.

The compound IX was therefore subjected to pyrolysis at 500° under the same conditions as used for the previous model compounds, and, as had been expected, it was found that rearrangement had occurred, and the isomer 2-benzoylacetaldehyde (X), was readily isolated and identified. In addition to the unchanged ester, the pyrolysate was found to contain cyclohexanone. This is a most surprising product, and since it does not appear to be possible to account for it by any known type of molecular scission, it may well be that a radical reaction is involved. However, since the source of this cyclohexanone might in fact be either of the two isomers (X or IX), it seemed desirable to ascertain which isomer had in fact been responsible.

The pyrolysis of the diketone X proved to be even more surprising than the results above, because it was found that

another rearrangement had occurred, yielding the original ester, IX. It was therefore quite clear from this result that the rearrangement originally found to occur with IX was in fact reversible, thus:



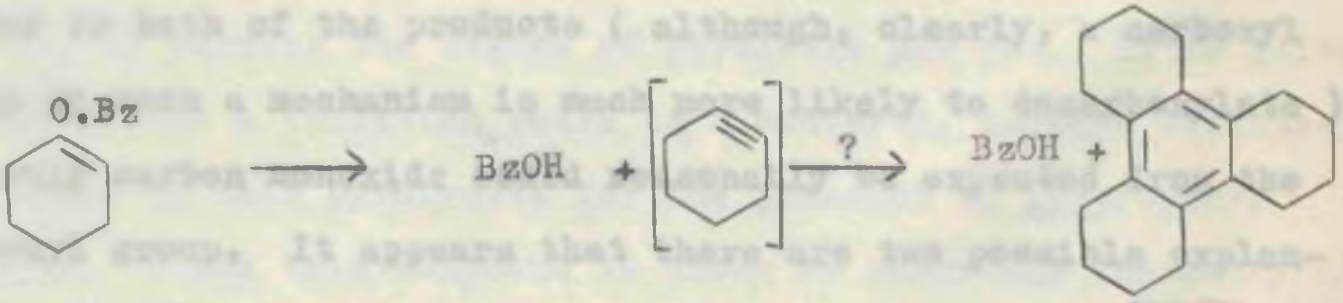
(IX) (X)

It follows, therefore, that any new compound formed during the pyrolysis of either IX or X cannot, without further evidence, be attributed positively to breakdown of IX only, or of X only. Since both of these are present, in equilibrium, in the vapour-phase, each must be taken into consideration as a possible source of any secondary products identified.

Yet another product which could not be explained by any direct molecular scission was discovered, this time in the pyrolysate from X. This product was benzene, which was present in only very small amounts, and, in fact its detection was possible by spectrographic means only. The pyrolysate from X also contained cyclohexanone, with the result that it is quite impossible to decide what is the source of either of these two products. In view of these difficulties, it is perhaps best to regard a radical mechanism as being the most likely way in which these otherwise inexplicable products could have been

formed. It is worthwhile noting that these two unexplained products represent the two " halves " (i.e., aromatic and alicyclic) of either IX or X and it is for this reason that a radical mechanism is preferred, although as yet it has not been possible to envisage any particular scheme which will explain the above products.

In the course of repeatedly pyrolysing IX as a method of preparing X for further study, it was noticed that a small amount of solid, readily soluble in the enol ester (IX), was being separated on fractional distillation. This amount was only very slight, and probably would not have been discovered had not this technique been applied. The substance was identified as benzoic acid, and may be evidence for a minor A^2 scission of IX (88):



XXXIV

If this is so, the acid should be accompanied by the alkyne cyclohexyne; but it is known (89) that this substance is too unstable for free existence, and would certainly undergo some secondary change during the pyrolysis, perhaps to a trace of dodecahydrotriphenylene (XXXIV), though this was not

actually observed in the pyrolysate.

3.3.2 : The relative composition of the gas pyrolysates.

A most surprising effect has been observed over the series of pyrolyses of both isomers. It has been found that the CO : CO_2 ratio in the pyrolysate increases as the extent of pyrolysis of the ester IX is increased; conversely, the ratio decreases as the extent of the pyrolysis of the diketone is increased. This result seems to be quite the opposite of what might have been predicted, since it is the ester IX which contains the carboxyl group (whence carbon dioxide would be expected), and it is the diketone which contains the isolated carbonyl group (whence carbon monoxide would be expected). If the decarboxylation and decarbonylation involved is of a molecular mechanism, then only the carboxyl group could yield either or both of the products (although, clearly, a carboxyl group by such a mechanism is much more likely to decarboxylate), and only carbon monoxide could reasonably be expected from the carbonyl group. It appears that there are two possible explanations for this result.

Firstly, if the mechanism is molecular, the apparent contradiction could be the result of the reversible rearrangement which has been shown to occur with the two isomers. The objection to this is that it implies that the pyrolysate is less stable than the pyrolysand. Since the isomer which is the pyrolysand

of one reaction is the pyrolysate from the other, this seems most improbable. Secondly, since there has already been evidence of a radical reaction, it may be that such a mechanism could explain this result (e.g., cf. the explanation given by Hurd and Blunck (5) for the products of methyl phenylacetate, which has been quoted in section 1.1.3).

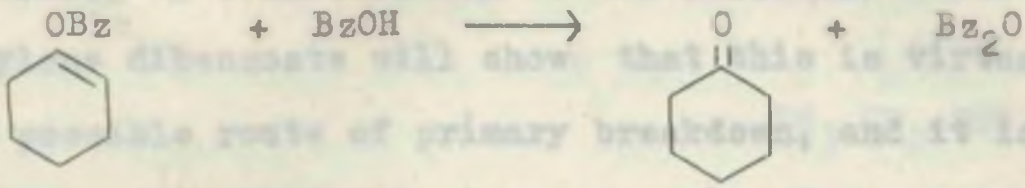
3.3.3 : The pyrolysis of acetylacetone (XI).

Because of the surprising results reported above (3.3.2), a simple β-diketone was chosen, acetylacetone (XI), to see whether carbon monoxide or dioxide would predominate in the gaseous pyrolysate. It was found from a single experiment that the monoxide was present in the greatest quantity (4.5 : 1), as would have been expected. A series of experiments would be necessary, however, to discover how the ratio was affected, if at all, by varying the degree of pyrolysis per run. It is quite possible that a variation would be discovered, because evidence was found in this pyrolysate for the presence of isopropenyl acetate. Since this compound is known to rearrange thermally to XI, it again appears that this type of rearrangement is also reversible.

3.3.4 : The reaction of cyclohex-1-enyl benzoate and benzoic acid.

To complete the comparison of the behaviour of the enol ester IX with vinyl benzoate, benzoic acid has been reacted with IX under prolonged reflux. The resultant mixture has shown the

presence of both cyclohexanone and benzoic anhydride:



IX XIX XX

Since, however, the possible amount of benzoic acid produced in the pyrolysis of IX is very small, this reaction does not appear to have occurred on pyrolysis. Furthermore, no trace of benzoic anhydride has been found in the pyrolysate of IX. This result, however, is interesting, since it shows that this type of reaction is more general than at first thought.

3.4 : Trimethylene dibenzoate (XII) and its products of pyrolysis.

3.4.1 : Disproportionation reactions in the pyrolysis of diesters.

It has already been shown that an important route in the pyrolysis of ethylene dibenzoate (II) is the D route, yielding acetaldehyde and benzoic anhydride (section 3.1.3), and it has been shown that originally these products were considered to result from a direct ester disproportionation. While it is now known that this is not likely to be the route involved, at the initial stages of this investigation there was no evidence to the contrary.

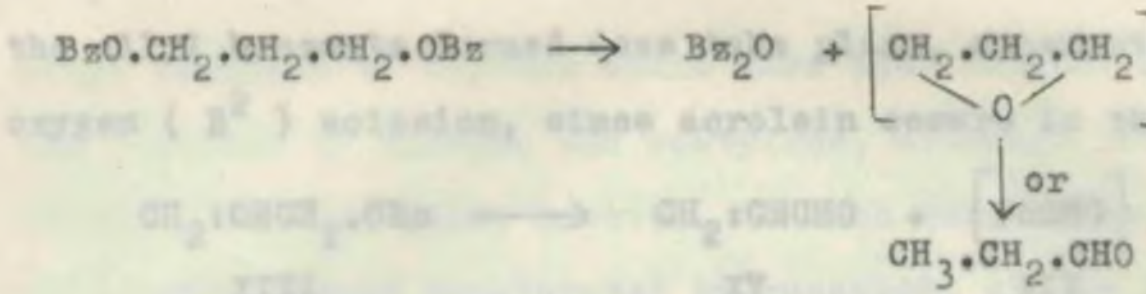
In support of this first theory, it had been shown (91) that methylene dibenzoate pyrolyses at 500° yielding, to a

large extent, formaldehyde (or its polymers) and benzoic anhydride. A consideration of the molecular structure of methylene dibenzoate will show that this is virtually the only possible route of primary breakdown, and it is therefore fairly certain that this is an example of an ester disproportionation:

$$BzO.CH_2.OBz \longrightarrow Bz_2O + H.CHO \quad ...D$$

It is not, however, at all certain just how such a reaction does occur, and possibly, at this stage, the most acceptable concept is a bimolecular reaction of some kind.

Because of this evidence, therefore, it was thought that the most likely mechanism for the D reaction in ethylene dibenzoate would be of the same nature. In fact, it seemed possible that this might be a general reaction for straight chain diesters, where the glycol, or alkylene, unit was capable of forming an aldehyde. It is also possible that the aldehyde is not formed directly, but is instead the rearrangement product of an alkylene oxide, which itself could be the true product of the disproportionation. Clearly then, if this reaction were general for most alkylene diesters, a notable example would be trimethylene dibenzoate (XII), which should yield propionaldehyde or propylene oxide:



It has, however, been shown that this is not the case, since neither propylene oxide nor propionaldehyde was isolated, and, although a little benzoic anhydride was found to have been produced, the absence of the other products proves that the D route does not occur here. Furthermore, this result emphasised the objections to applying the D route directly to explain the products of ethylene dibenzoate, and it was therefore on the basis of this that a new explanation was sought, and found. This explanation has been dealt with in some detail in an earlier section (3.1.3).

3.4.2 : The products of pyrolysis of trimethylene dibenzoate.

Trimethylene dibenzoate appears to crack by one primary route only; an alkyl-oxygen scission (A^1) yielding allyl benzoate (XIII) and benzoic acid (XIX):

This suggests that the β-methylene group alone takes part since none of the other possible isomers of XIII are formed. It also indicates that, under the conditions of experiment, no form of allylic rearrangement is in evidence. Secondary pyrolysis of

the allyl benzoate formed does take place, apparently by an acyl-oxygen (B^2) scission, since acrolein occurs in the pyrolysate:

$$\underset{\text{XIII}}{CH_2{:}CHCH_2.OBz} \longrightarrow \underset{\text{XV}}{CH_2{:}CHCHO} + \underset{\text{XIV}}{\left[PhCHO\right]} \quad \ldots B^2$$

Nevertheless, there was no sign of benzaldehyde, which should formally have accompanied the acrolein. To explain this, therefore, a pure sample of XIII was pyrolysed, whence it was discovered that only slight pyrolysis had occurred, and that any benzaldehyde formed had again suffered complete destruction. This was surprising, particularily since it was found that benzaldehyde itself on pyrolysis under these conditions decomposed to only a very small extent. It therefore appeared that benzaldehyde should have survived pyrolysis. A further sample of XIII was accordingly pyrolysed, and to this there had been added some 5 % of benzaldehyde. After pyrolysis, it was found that only about a quarter of the benzaldehyde added could now be accounted for, which made it apparent that, for some reason, under these conditions the benzaldehyde produced by pyrolysis did not survive, and hence its absence.

Further examination of the allyl benzoate fraction has shown that it contained another unsaturated compound, which could be separated after hydrolysis of the ester. This compound has been identified as allylbenzene, and it is quite clear that this is a genuine example of ester decarboxylation. As stated previously (section 3.1.4) the suggested decarboxylation of

vinyl benzoate to styrene could have been brought about by the reaction of benzene and acetylene, although this seems unlikely. In this case, however, no such dubiety exists, since the corresponding unsaturated hydrocarbon, allene (or its isomer, methylacetylene) is not formed from XIII on pyrolysis (only the B^2 route has been found). While most other examples of ester decarboxylation have had the carboxyl group directly adjacent to an unsaturated grouping, in this example the position is β to the double bond. It is therefore difficult to assess fully what influence adjacent unsaturation has on decarboxylation, although it seems reasonable to suggest that there is some relation.

A further product has been discovered by infrared spectrography to be present in the pyrolysates of both trimethylene dibenzoate (XII) and allyl benzoate (XIII). It is therefore reasonable to conclude that its source is XIII, and that it is a product of that compound. The spectrum shows the characteristic absorption bands of an alcohol, together with bands which normally correspond to a vinyl compound. As yet, however, no satisfactory explanation or interpretation of these bands has been achieved.

Finally, it has been shown that benzoic anhydride is present, though it does not appear to be the product of a D route. The quantity involved is quite small, but as yet there has been no complete explanation for its formation.

3.4.3 : The gas pyrolysates of XII, XIII, and XV.

The infrared spectrum of the gas pyrolysate of XII was notable for an amount of absorption in the low energy region (700-1200 cm^{-1}). Since none of these absorption bands could be correlated with any known gases, it was considered that they might have arisen from some other compound produced in the pyrolysis. Of the possibilities, acrolein (XV) seemed the most likely, and it was accordingly pyrolysed under the usual conditions, and the gas analysed by infrared spectrophotometer. This spectrum was almost identical with the unexplained part of the spectra from previous pyrolyses (from XII and XIII), and it was therefore clear that these gases were the products of acrolein, and, as such, were not of great relevance to the study. It is interesting to note, however, that Thomson and Frewing (92) have studied the pyrolysis of acrolein, which, they state, pyrolyses by two routes, unimolecular (a), and bimolecular (b):

$$CH_2{:}CH.CHO \xrightarrow{(a)} CH_2{:}CH_2 + CO$$

$$CH_2{:}CH.CHO \xrightarrow{(b)} \tfrac{1}{2}\,(C_4H_8 + CO)$$

It is possible, therefore, that the unknown gas is a hydrocarbon (C_4) which is quite feasible from the evidence of the infrared spectrum.

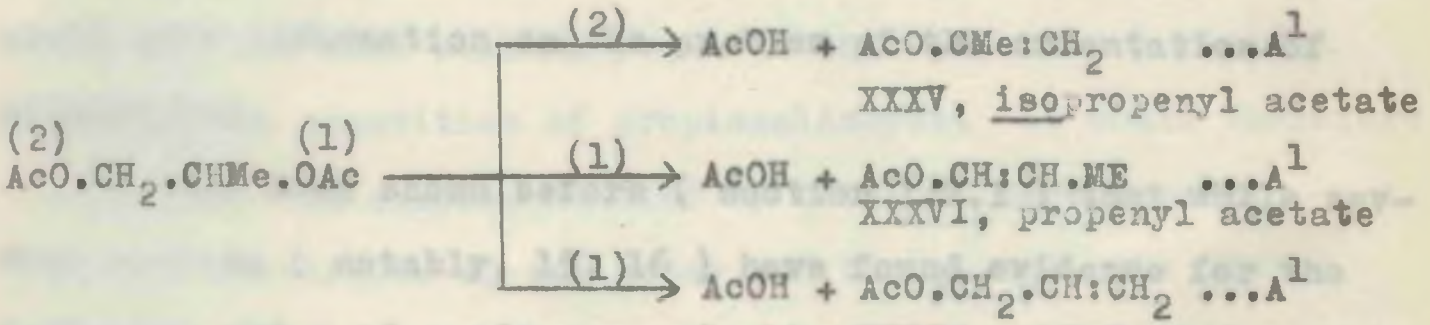
3.5 : The diesters of propylene glycol.

3.5.1 : The orientation of elimination in alkyl-oxygen scission.

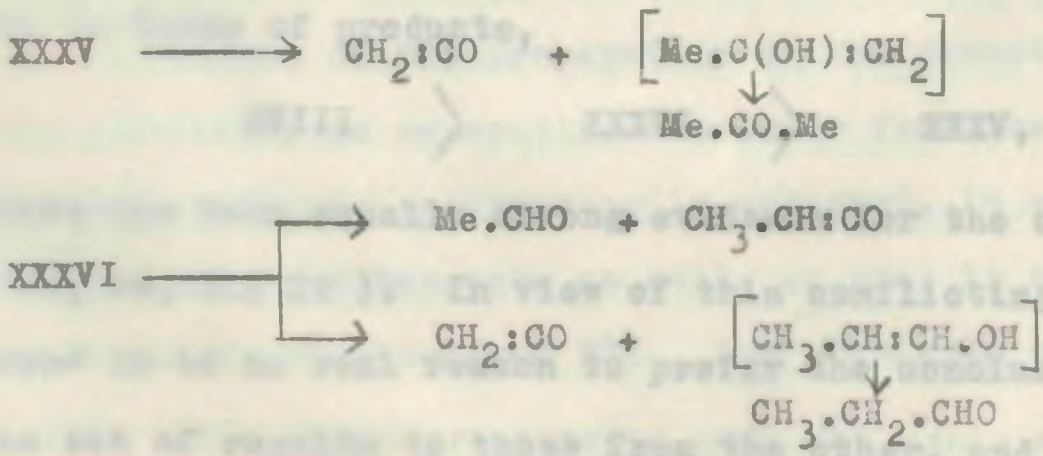
The studies which have hitherto been carried out on the pyrolyses of alkylene diesters (e.g., ethylene dibenzoate, section 3.1, and trimethylene dibenzoate, section 3.4) have been done with esters in which all the available β-hydrogen atoms have been exactly equivalent, and thereby indistinguishable. It therefore seemed that, while only these esters bore a direct relationship to the polyester I, it would be of considerable general value to study the pyrolysis of an ester in which the available β-hydrogen atoms did not all occur in equivalent sites.

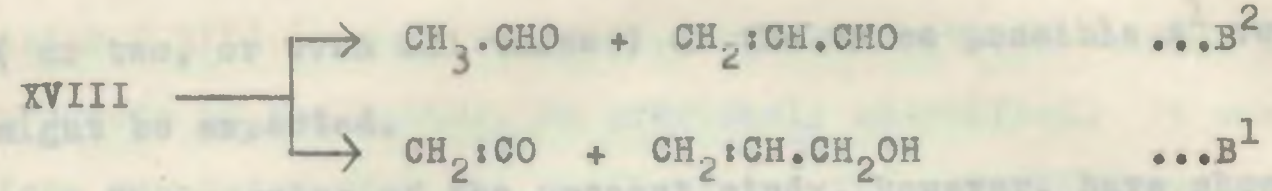
Although a considerable amount of work has been reported on this aspect (cf. section 1.1.2) these various results have in many cases been quite contradictory and it is very difficult to decide from the literature in what preferred sequence the differently substituted carbon atoms (methyl, methylene, and methylidyne) give up the available β-hydrogen atom. Accordingly, an ester which contains all three types of hydrogen-bearing carbon atoms has been chosen, viz., propylene diacetate (XVI). This has been found to be of considerable interest, particularly because a previous investigation has been reported (79) with results which are not consistent with any one alone of the three possible routes of decomposition (vide table of routes below), but rather a mixture of the products of two of

these routes, In this work, Chitwood has reported that XVI pyrolyses to give acetic acid, allyl acetate, and propionaldehyde. This result is of great interest, because, if all the theoretically possible routes of scission are detailed, it can be seen that the last two products, allyl acetate and propionaldehyde, must come by different routes. Thus, there are three different ways in which the initial A^1 scission can take place, and, thereafter each of the three isomeric esters so-produced can undergo a B type scission. All three are capable of the B^1 route, and two of these are capable of the B^2 route. There is thus a great variety of possible products, as shown below:



Thereafter, the possible products are:





These equations show that propionaldehyde if in fact found would be the product of a B^1 scission of XXXVI, propenyl acetate, and is not likely to be a product of XVIII, allyl acetate. It therefore seemed reasonable to wonder whether or not the product XVIII described by Chitwood was pure, and whether it did not in fact contain some quantity of its isomer, propenyl acetate, which would be most difficult to separate. It was for this reason that the pyrolysis of the diester, XVI was repeated, since it was clear that this would yield some information on the problem of the orientation of elimination.

It has been shown before (section 1.2.1) that while several workers (notably, 15, 16) have found evidence for the following order of preference of elimination of β-hydrogen atoms,

$$CH_3 \rangle CH_2 \rangle CH,$$

or, in terms of products,

$$XVIII \rangle XXXVI \rangle XXXV,$$

there has been equally strong evidence for the opposite (14, 20, 21, 22). In view of this conflicting evidence there seems to be no real reason to prefer the conclusions from the one set of results to those from the other, and so any one

(or two, or even all three) of the three possible A^1 routes might be expected.

The results of the present study, however, have shown that only one route occurs, yielding XVIII alone, and without any trace whatsoever of XXXVI or XXXV, as shown by spectrographic analysis. Furthermore, the aldehyde found was acrolein, and not propionaldehyde, which, as shown above, is the product to be expected from XVIII (cf. allyl benzoate, XIII, section 3.4.2). There were, however, faint traces of propionaldehyde (shown by the very sensitive paper chromatography technique), and it was found that on pyrolysis an impure sample of XVI (containing a quantity of propylene glycol, which has virtually the same boiling point as the diacetate) yielded considerable quantities of propionaldehyde. It would therefore appear that the samples handled by Chitwood were impure, probably azeotropes of the ester and the glycol, the latter being the source of the propionaldehyde reported by him.

3.5.2 : Other related results.

A feature of the preparation of the diacetate XVI has been the difficulty in separating the ester from the glycol, and although this was satisfactorily achieved, it was deemed wiser to prepare the dibenzoate as well, so that it could serve as a check on the results from XVI. The pyrolysis of the dibenzoate (XVII) was therefore carried out, and again only the allyl

ester (XIII) could be found, together with the appropriate products of the latter, as previously identified. It was therefore concluded that the pyrolysis of XVI and XVII involved the preferential abstraction of a β-hydrogen atom from that carbon atom which contained the greatest number of β-hydrogen atoms, in this case the methyl carbon atom. It might therefore appear that an ester containing a β-methyl group on the alkylene chain would possess less stability than one which did not have such a substituent.

Finally, to complete this investigation, the pyrolysis of allyl acetate (XVIII) has been carried out, and it was confirmed that this underwent a B^2 scission, of which the first product, acetaldehyde, did not survive, but underwent further pyrolysis:

$$\text{XVIII} \longrightarrow \underset{\downarrow \text{XXI}}{[CH_3CHO]} + \underset{\text{XV}}{CH_2{:}CH.CHO} \quad \ldots B^2$$

$$CH_4 + CO \quad \ldots C^1$$

The gas infrared spectrum was found to contain bands corresponding to methane, and also the range of absorption maxima related to the products of acrolein, XV (cf., section 3.4.3), but there was also present a system of broad absorption maxima, which has been attributed to butene-1. Since this was not produced in the pyrolysis of XV (which is reported to pyrolyse to some C_4 unsaturated hydrocarbon), it is

presumably a genuine product of XVIII, and therefore seems to be another example of ester decarboxylation:

$$\text{XVIII} \longrightarrow CH_2{:}CH.CH_2.CH_3 + CO_2 \quad \ldots C^2$$

This is completely parallel to the decarboxylation of allyl benzoate (cf., section 3.4.2) and presumably therefore it is a feature of allyl esters that they possess the ability to decarboxylate.

4 : General Assessment of Results.

In the preceding sections the importance and relevence of the individual results has been discussed as fully as possible within the actual context. In conclusion, therefore, the main postulates of this thesis have been assembled and considered under four sub-divisions, and these are discussed below.

4.1 Quite the most significant result has been the discovery that vinyl esters rearrange first to a β-ketoaldehyde, which thereupon undergoes decarbonylation. This result is of great relevence to the study of the breakdown of poly(ethylene terephthalate) because it has been found to occur with the vinyl esters of both benzoic and terephthalic acids. Thus, while the model compound III, vinyl benzoate, indicated in the first place the existence of this reaction, it has been necessary to demonstrate the capability of a vinyl terephthalate to undergo this type of rearrangement before the parallel could be safely and conclusively drawn for the polyester. In actual fact, although this has not been demonstrated by the direct study of a vinyl terephthalate, the method of approach (i.e., by using the model VII, 2-benzoyloxyethyl terephthalate) has been through a model bearing a truer, more direct, and more obvious relationship to the polyester than that of any chosen vinyl terephthalate.

It therefore seems quite feasible to predict that the

polyester will degrade by random scission to give fragments yielding ketonic products. Already it has been shown (76-78) that the polyester does not pyrolyse to yield vinyl esters, and the reason for this complete absence in the above studies has been shown in an earlier section (3.1.2) to be the result of the prolonged contact-times of these experiments. The relationship of this reaction with time and temperature has been clearly demonstrated (loc. cit.) and it has thus been possible to understand fully the existing results.

With regard to these findings, two previously unexplained results are worthy of mention. Firstly, Gilchrist and Ritchie (78) found evidence for the presence of ketonic products in the pyrolysate of poly(ethylene terephthalate), and although they were unable to provide any identification of these products, it is significant that their presence was noted. Secondly, Chitwood (79) has reported the presence of ethyl methyl ketone in the pyrolysate of ethylene dipropionate, and this, clearly, may be explained by the R/C^1 breakdown of vinyl propionate.

There are now, therefore, sufficient examples of the vinyl ester type of rearrangement to predict that this is a general reaction (86), although it is also clear from this present work that the full R/C^1 reaction is restricted entirely to vinyl esters.

4.2 The study of the thermal rearrangement of cyclohex-1-enyl

benzoate has revealed a feature of this type of reaction which has not hitherto been reported. This is the reversibility of the rearrangement, and in the light of this result it may be necessary in the future to review the existing results of the pyrolyses of those β-diketones which are analogous to 2-benzoyl-cyclohexanone. While the original purpose of this investigation of the pyrolysis of the enol benzoate has been achieved (viz., to discover if it underwent thermal rearrangement), it has become clear that the complete pattern of decomposition is considerably more complex than originally envisaged. This is partly the result of the rearrangement being reversible, because the presence of both isomers in the pyrolysate of either of them precludes the proper deduction of the source of any other products. Since it has not been within the scope of this present study to consider this aspect in fuller detail, it has not been possible, therefore, to present any evidence for the manner of production of such products as cyclohexanone and benzene. It is, however, quite clear that these compounds are not produced by any known or simple molecular scission, and it is considered that a radical mechanism would be a more acceptable postulate.

As indicated in section 3.3.3, there is also evidence for the reversibility of the rearrangement of isopropenyl acetate to acetylacetone, and it is therefore felt that the reversibility of such rearrangements may be quite general to this class of

compound. Again, however, it has not been within the scope of this present work to carry the investigation any further in this direction.

4.3 The pyrolytic disproportionation of esters has been discussed in a previous section (1.1.5), and it has been noted that a result of disproportionation is frequently an increase in molecular symmetry. In fact, it might be said that there are no true examples in the literature of the disproportionation of a completely symmetrical ester (or, in point of fact, diester). Thus, the example provided by Jones and Ritchie (91), methylene dibenzoate, appears to be a genuine disproportionation, but this ester could not be truly called symmetrical (i.e., it could not be visualised as being split into two exactly equal radicals or halves). While an intermolecular reaction has been proposed (section 3.4.1) as being the most likely for this disproportionation, the actual mechanism is still obscure. However, it was originally felt that by whatever means this mechanism took place, by the same means would the known " disproportionation " of ethylene dibenzoate occur. If, therefore, this was the case, then it would have been possible to predict equivalent results in the disproportionation of trimethylene dibenzoate.

Since, however, this last example did not exhibit this reaction, it became clear that the whole conception of ester disproportionation was incorrect. This has subsequently been

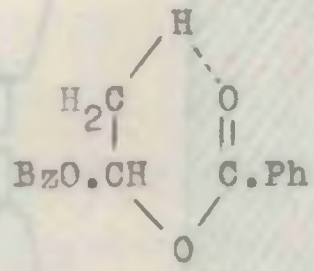
proved conclusively by the discovery of an alternative mechanism for the disproportionation of ethylene dibenzoate, and it is now clear that a parallel disproportionation to that of methylene dibenzoate has only been found in the pyrolysis of 2-benzoyloxyethyl terephthalate. This new mechanism operates by the reaction of benzoic acid and vinyl benzoate to yield the intermediate ethylidene dibenzoate, which does not survive itself but further decomposes to yield benzoic anhydride and acetaldehyde. It is therefore readily understood why trimethylene dibenzoate does not undergo a comparable reaction, since the products of A^1 scission, allyl benzoate and benzoic acid, are apparently incapable of this reaction.

This new light on the disproportionation of symmetrical esters should be of considerable value in the future in the interpretation of the pyrolysis results of related esters, and also polyesters. Thus, genuine ester disproportionation may be expected from polyesters, but only when " asymmetry " is giving place to " symmetry ". If this is not the case, then simple molecules alone (presumably) will be the source of any other " disproportionation " reactions, and these should give rise to acetaldehyde and an acid anhydride. Since such groupings have been reported (76-78), this may well represent the true position.

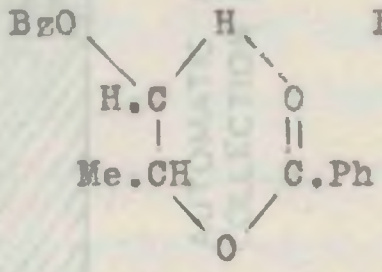
4.4 Throughout the preceding sections the important relationship which the β-hydrogen atoms bear to the pyrolysis

of a carboxylic ester has been stressed. It has been shown that the availability or absence of these atoms can determine the route by which pyrolysis will occur. However, in all those models which bore a direct relationship to the polyester, the available β-hydrogen atoms, where there were more than one, all held completely equivalent positions. In order to determine, therefore, what would happen when there was competition from different sites which were not equivalent, the pyrolysis of the diesters of propylene glycol was carried out. This indicated that of the three possible sites, the one richest in hydrogen atoms, viz., the methyl, was the one which lost the β-hydrogen atom. This is in striking agreement with the results of Bailey et al., (15, 16), although as stated in section 1.1.2, they are in complete contrast to the behaviour of menthyl esters noted by several other workers (inter al., Barton et al., 14, 20, 21). However, it seems quite feasible to suggest that the precedence observed in the propylene diesters will also obtain in polyesters where a similar choice exists in the supply of β-hydrogen atoms. Although the true explanation for the preferential abstraction of the hydrogen atom from the methyl group is lacking, the proposed chelate structure of Hurd and Blunck (5) is useful by way of forming a tentative explanation for this result. This chelate structure has been shown in section 1.1.2, and if it is applied in turn to the three possible methods of β-hydrogen atom abstraction, it can been seen that the one involving the methyl

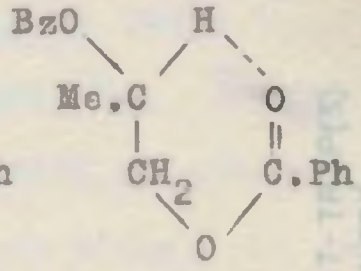
group is probably less hindered than the other two. Hence, from these structural models it would appear that the greatest ease of formation of an hydrogen bridge will be found in this one.



(a)

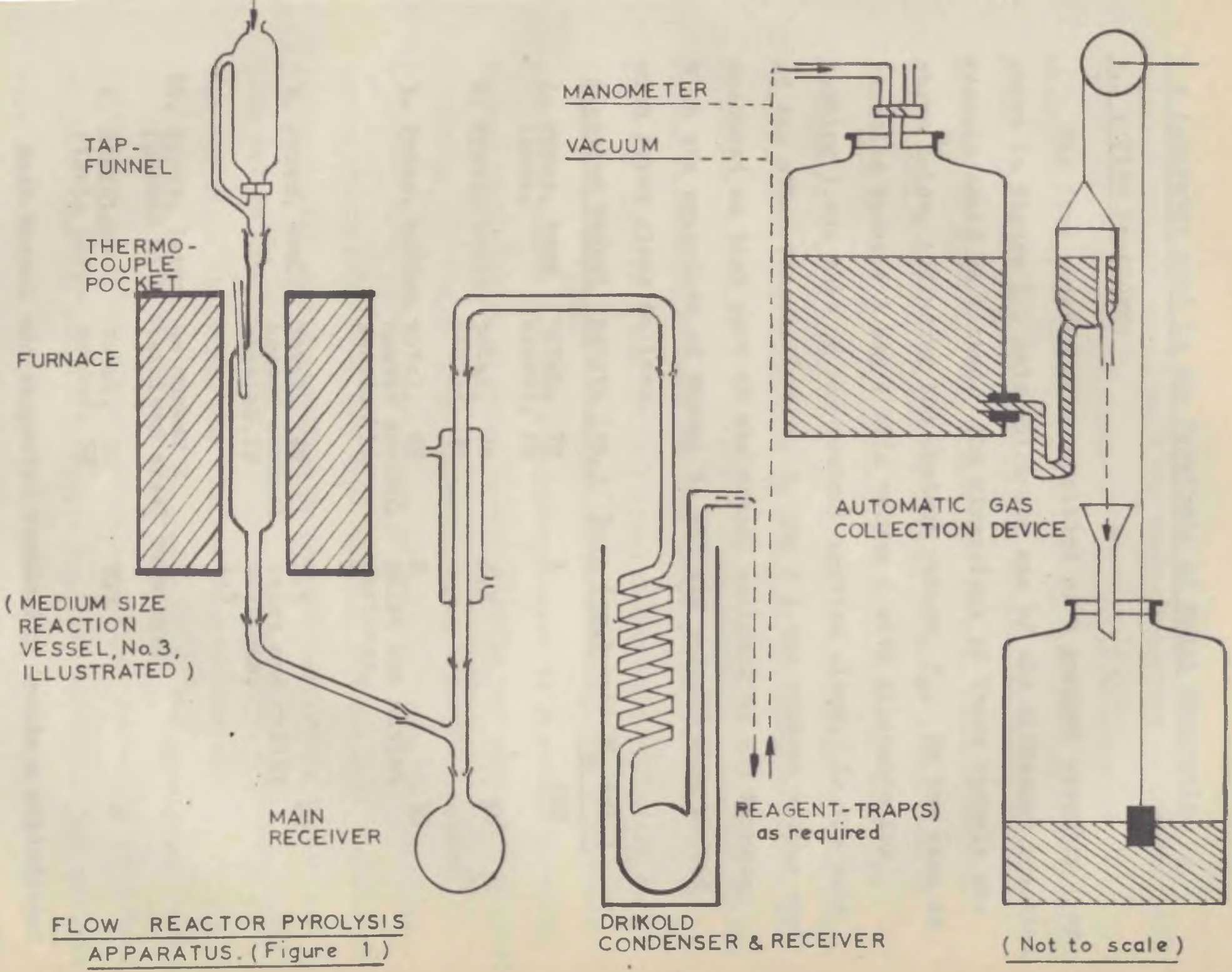


(b)



(c)

β-Hydrogen atoms from (a) methyl (b) methylene and (c) methylidyne groups.



FLOW REACTOR PYROLYSIS APPARATUS. (Figure 1)

5 : Apparatus used in the Pyrolysis of Model Compounds.

5.1 : Flow Reactors.

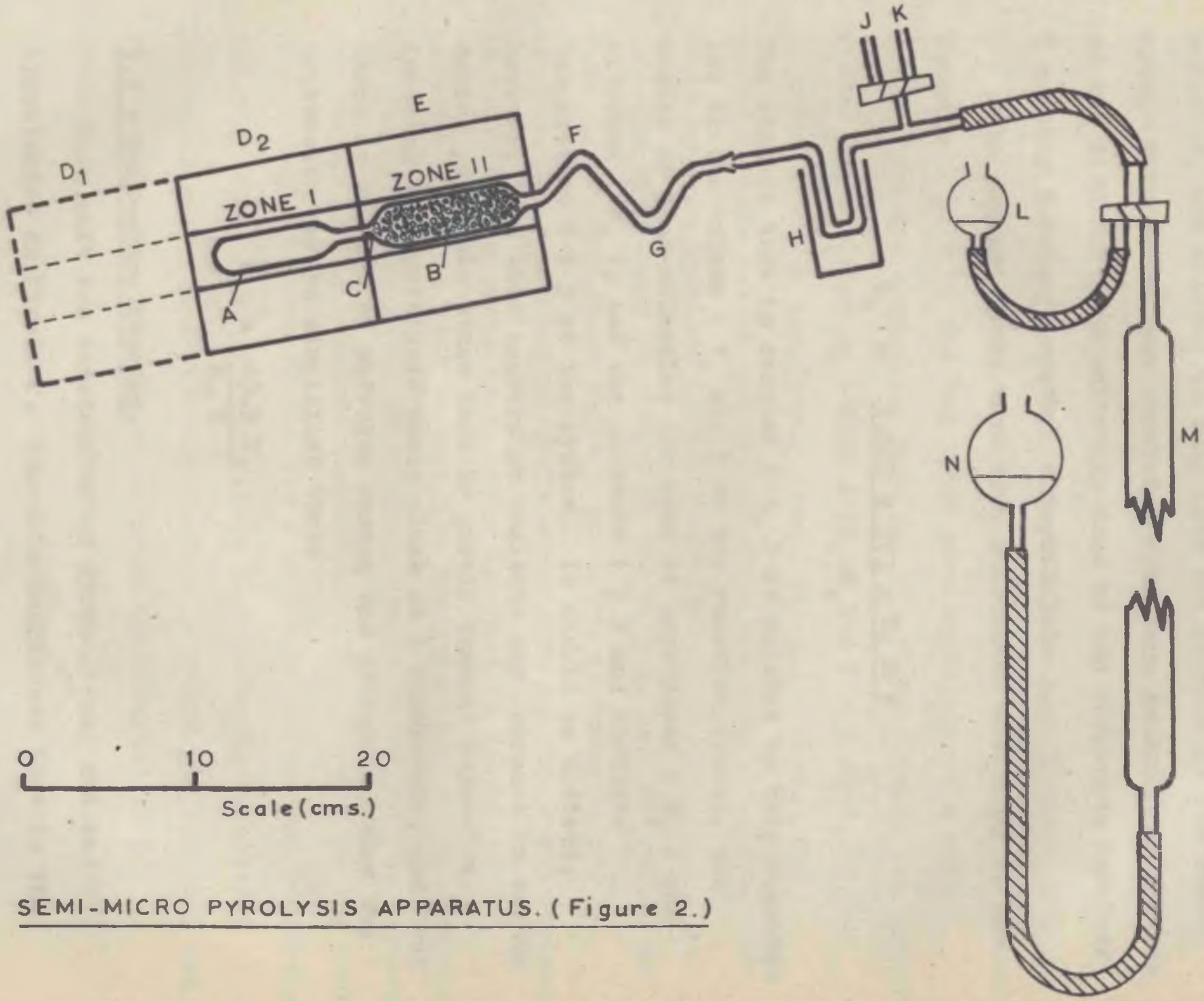
The flow reactor unit consisted of a general assembly (as shown in Figure 1) into which any one of six different reaction vessels could be fitted. The dimensions of these vessels are shown below, including the contact volume, V_c. In the case of reaction vessels 3 and 4 this volume (with allowance for packing) was that of the central section alone. In the case of the other vessels (1, 2, 5, and 6) the contact volume was measured as that part of the vessel enclosed by the furnace. With the exception of vessel 5, all the vessels were packed with Pyrex glass helices.

Reaction vessel	Length (cm.)	Bore (cm.)	V_c (ml.)
1. Pyrex, very large.	total, 70 heated, 40	3	220
2. Pyrex, large.	total, 70 heated, 30	2.3	50
3. Pyrex, medium.	total, 65 heated central section, 18	2 inlet and outlet sections, 1	30
4. Pyrex, small.	total, 40 heated central section, 12	2.5 inlet and outlet sections, 1.5	20
55. Pyrex, large. (packed with stainless steel turnings)	as number 2		
6. Stainless steel, large.	total, 70 heated, 50	2.3	-

Each vessel was supported vertically inside a cylindrical

electric furnace, which kept the central section of the reaction vessel at a temperature controlled ($\pm 5^{o}$) by a series of resistences and an energy controller and measured by a chromel-alumel thermocouple located axially within the reaction vessel. Before each pyrolysis the system was several times evacuated and filled with oxygen-free nitrogen, to avoid combustion of the vapours. Liquid pyrolysands (which, however, were not out-gassed) were introduced by either a tap-funnel or a syphon-funnel fitted with side arms to equalise the pressure above and below the feed-liquid. In the case of solids, these were melted in the tap-funnel using a heating jacket, and then run in as liquids. Liquid (and solid) pyrolysates were collected in a first receiver, *via* an inclined air-condenser. The exit-gases were then passed through a water-condenser to a second receiver cooled in a mixture of solid carbon dioxide and acetone (Drikold condenser). The final uncondensed gases were then passed (through specific reagent-traps as required) to an automatic device which collected them over water (covered with a layer of gas-saturated liquid paraffin to prevent absorption of the gas). This device maintained the system at atmospheric pressure, and any deviation therefrom was visible on a manometer.

In one specific case (pyrolysis 33), the pyrolysand was introduced in pellet-form, the pellets being contained in a tube of just slightly greater diameter inclined upwards. The pellets were propelled up the tube by an iron rod, activated by a



SEMI-MICRO PYROLYSIS APPARATUS. (Figure 2.)

solenoid, and allowed to drop into the furnace at the chosen rate. This method was precluded from more general use because of the difficulty in pelleting some of the compounds involved (notably 2-benzoyloxyethyl terephthalate).

The contact times have been calculated according to the formula

$$t_c = \frac{3.600 \times 273 \times V_c \times p}{22.4 \times (N_v - N_n) \times T}$$

The contact time in seconds (t_c) is related by this expression to the volume (V_c ml.) of the reaction vessel, the number of gram-molecules per hour of pyrolysand (N_v) and nitrogen (N_n), and the pressure (p) and absolute temperature (T) of the system. It should be noticed, however, that this expression neglects any increase in volume during pyrolysis other than by purely thermal expansion. Assuming that pyrolysis takes place at 1 atmosphere, and that there is no flow of nitrogen during the pyrolysis, then the expression may be simplified thus:

$$t_c = \frac{43.9 \, V_c}{N_v \, T}$$

5.2 : Semi-micro Reactor.

This unit was constructed of Pyrex glass, and is illustrated in Figure 2. Its main usefulness lies in the ability to study the gas pyrolysate from only a very small

amount of pyrolysand. It was found by experiment that the optimum quantity of pyrolysand was 300 mg., and, with the exception of three pyrolyses (22, 26, and 28), this has been the amount used. The reaction vessel consists of three zones; the first zone containing the bulb A, the second zone containing the packed bulb B, and the third zone containing the reflux bend F, and the condensing bend G. The first furnace can occupy either the position D_1 to the left of the first zone, or the position D_2 which completely covers the first zone. The second furnace covers the second zone, and does not move. The whole unit is inclined slightly upwards.

The pyrolysand is placed in the bulb A, and the bulb B is then filled with glass beads (ca. 3 mm. diameter), the constriction C preventing their entry into A. The first furnace is initially in position D_1 while the unit is assembled and asbestos fibre is used to insulate the open ends of the furnaces. The trap H is cooled in Drikold/acetone mixture, and the furnaces are heated to the required temperature. The mercury in the limb M is raised by means of the leg N to above the two-way stopcock, which is then shut, and thereafter the system is repeatedly evacuated and filled with oxygen-free nitrogen via inlets J and K. Finally, the pressure of nitrogen is adjusted to 1 atmosphere, and the unit is then isolated after which the stopcock leading to the gas reservoir (M) is opened. The first furnace is introduced over the first zone slowly and

regularily, this operation taking a predetermined time. When it is in position D_2 it is kept there for the desired time, and, as pyrolysis proceeds, the barometric leg N is adjusted to keep the pressure at 1 atmosphere. In most pyrolyses the bends F and G were kept in the position illustrated, but the whole tube could be inverted, thus reversing the functions of these bends (*vide* pyrolysis 30). At the end of the pyrolysis the first furnace was returned to position D_1 , and the first zone allowed to return to room temperature, whereupon the pressure was adjusted to 1 atmosphere. It was now possible to read from the gas burette the quantity of gas that had been evolved during pyrolysis. Thereafter, *ca.* 80 % of the gas was collected by lowering the level of the mercury in the limb M before shutting the stopcock. This gas was then analysed by Sleigh's method (107), the leg L being used to sweep out all the connections before transferring the gas. From the capacity of the reaction vessel (29 ml.) the total gas evolved could be calculated.

6 : Preparation of Model Compounds.

Where the method of identification of compounds is repeated in subsequent preparations or experiments, the constants are not generally quoted more than once, unless they are of special significance. All melting points have been confirmed by mixed melting test where possible. Where constants have been quoted, the corresponding constants in the literature have been appended in parentheses.

6.1.1 : Ethylene dibenzoate (II).

Ethylene glycol was benzoylated in acetone solution, and the product precipitated by the addition of potassium hydroxide solution. The crude ester was recrystallised from benzene, m. 72-3° (73°).

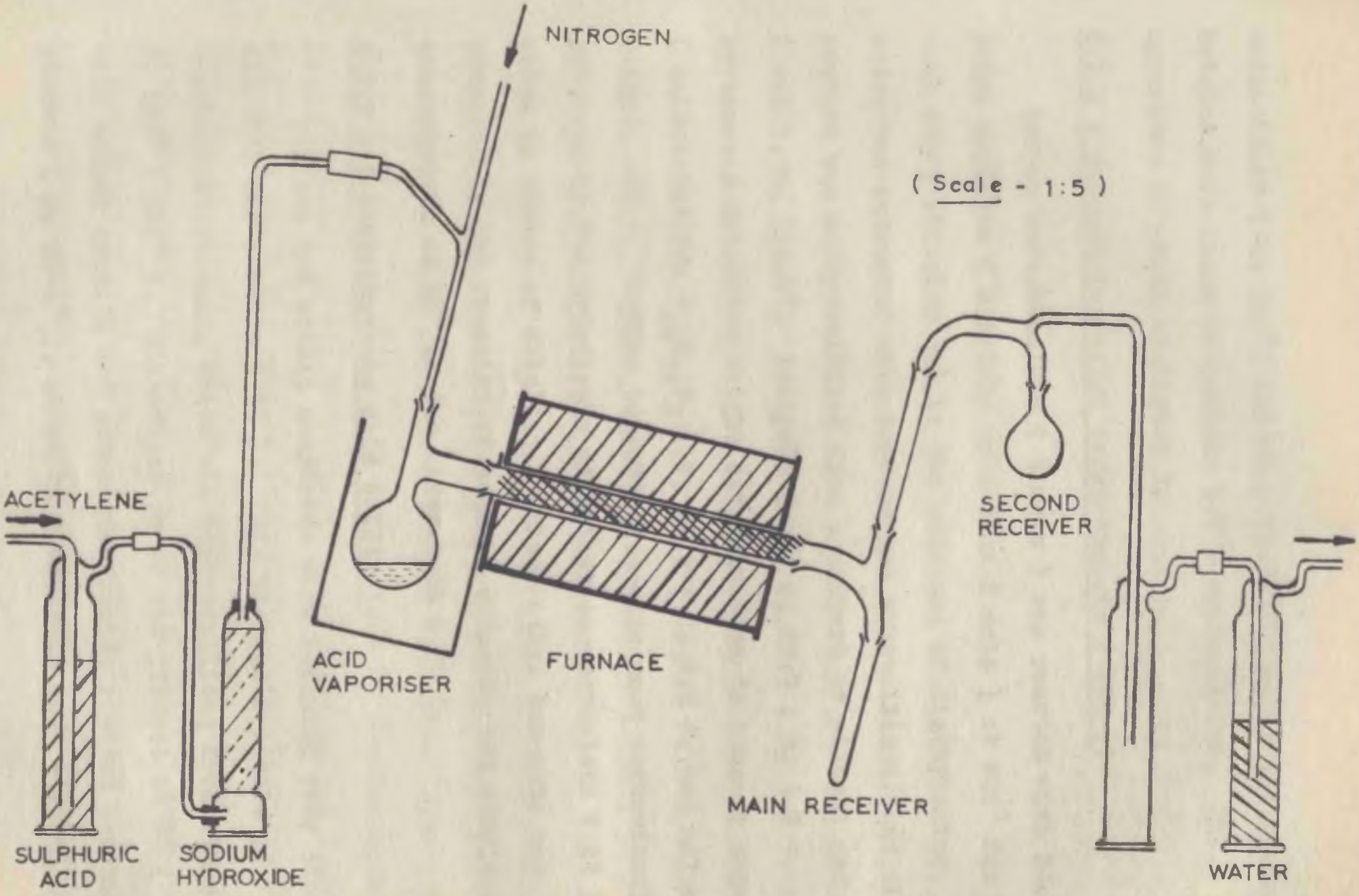
6.1.2 : Benzoylacetaldehyde (IV).

Ethyl formate (1.5 mole) and acetophenone (1 mole) were treated with sodium ethoxide (0.5 mole) in dry ether (100 g.) as described by v. Bulow and Sicherer (93). This yielded the sodium salt of IV which was converted into the sparingly soluble copper salt. This was filtered and then carefully washed with water and then ether, and cautious acidification with cold dilute mineral acid yielded IV. Three separate preparations gave slightly impure IV, but all three gave concordant analyses (found : C, 74.3 ; H, 5.7 % ; equiv-

alent by alkaline hydrolysis, 175. Calculated for $C_9H_8O_2$: C, 73.0 ; H, 5.4 % ; equivalent 148). The compound was characterised as its phenylhydrazone (which is a mixture of isomers), m. 124-6° (decomposed). v. Auwers and Schmidt (94) quote m. 126° (decomposed), and analysis found N, 11.9 % (Calculated for $C_{15}H_{14}ON_2$: N, 11.8 %). The compound is very unstable, and cannot be purified by distillation in vacuo. A small fraction (20-30 %) can be distilled at 94-98°/ 1 mm., but this does not change the analysis (found : C, 74.3 : H, 5.8 %). Thereafter, further distillation produces water and at least 33 % of the batch becomes completely resinified. The compound was heated for a period in an atmosphere of nitrogen, after which it was possible to separate crystals of 1:3:5-tribenzoylbenzene, m. 116-7° (from ethanol; Claisen, 95, quotes m. 118°). This is a known condensation product of IV, and analysis found C, 83.4 ; H, 4.8 % (Calculated for $C_{27}H_{18}O_3$: C, 83.1 ; H, 4.7 %). Calculations based on these analytical figures and equivalent weight suggest, therefore, that the crude benzoylacetaldehyde contains 11-13 % of this triketone.

6.1.3 : Vinyl benzoate (III).

Acetylene reacted with benzoic acid in the gas phase at 300-350° over a catalyst (96). The catalyst is a mixture of zinc, cadmium, and mercuric chromite. The product was



APPARATUS for the PREPARATION of VINYL ESTERS. (Figure 3.)

redistilled (b. 203°/ 760 mm., 72-74°/ 3 mm.) and various batches were found to contain 1-7 % acetophenone. The apparatus is shown in Figure 3.

6.2.1 : 2-Benzoyloxyethyl terephthalate (VII).

Sodium terephthalate (1 mole) was reacted with 2-chloroethyl benzoate (slightly more than 2 mole) at 200° for 5 hours with rapid stirring and in the presence of diethylamine. The ester was extracted with benzene and crystallised, and this product was recrystallised from a mixture of ethanol and methanol (4:1), m. 114-5°. Analysis found C, 67.7 ; H, 4.9 %, and cryoscopic molecular weight determination in benzene gave 471 (calculated for $C_{26}H_{22}O_8$: C, 67.6 : H, 4.8 %, and molecular weight, 462). Sodium terephthalate was most conveniently obtained by the hydrolysis of methyl terephthalate (97) using an excess of alkali. 2-Chloroethyl benzoate was prepared by the reaction of benzoyl chloride and ethylene chlorohydrin at 60° on the water-bath (98).

6.2.2 : 4-Acetylbenzoic acid (VIII).

Aniline and acetic anhydride were refluxed over zinc chloride for 4 hours (99). This yielded crystals of 4-aminoacetophenone, which was recrystallised from ethanol, m. 103° (106°). Diazotisation of the product at 0° (100) with copper cyanide and potassium cyanide yielded 4-cyanoacetophenone (m. 60-1°), which on hydrolysis with alcoholic

potassium hydroxide solution yielded VIII. The product was recrystallised from water, m. 200° (Ahrens, 100, quotes the m.p. at 200°, but Fichter and Meyer, 101, quote 208°). The substance gives a 2:4-dinitrophenylhydrazone which sinters at 280° (not quoted).

6.3.1 : cyclohex-1-enyl benzoate (IX).

The enol benzoate of cyclohexanone has not been prepared directly, and must therefore be obtained by ester interchange via the readily prepared enol acetate. The most convenient method of preparing cyclohex-1-enyl acetate has been found to be by the reaction of cyclohexanone and acetic anhydride in the presence of p-toluenesulphonic acid (102). The product has a characteristic odour, and is a colourless liquid, b. 176-9°/ 760 mm. (Bedoukian, 102, quotes b. 180-2°/ 760 mm.).

The cyclohex-1-enyl acetate was added to an aqueous solution of mercuric acetate (103) giving an immediate exothermic reaction. To this solution was added finely powdered potassium chloride, which gave a white precipitate of 2-chloromercuricyclohexanone, m. 134-5° (134-5°), recrystallised from water. The dried solid was reacted in equimolar quantites with benzoyl chloride in xylene, and the mixture was kept at 50° for 12 hours with rapid stirring. Fractional distillation in vacuo yielded a main fraction, b, 148-54°/ 3 mm. This fraction had a fine suspension of mercuric chloride which was easily removed by

washing with dilute ammonia. The purified substance was a colourless liquid, b. 148-52°/ 5 mm. (b. 146-7°/ 6 mm.). The substance was identified and characterised from the products of acid hydrolysis, and analysis found, C, 77.2 ; H, 7.23 % (calculated for $C_{13}H_{14}O_2$: C, 77.2 ; H, 6.98 %).

6.4.1 : Trimethylene dibenzoate (XII).

Trimethylene glycol was benzoylated in acetone solution, and the product separated as a yellow oil on the addition of potassium hydroxide solution. The separated oil crystallised, and was then recrystallised from light petroleum (b. 60-80°) containing a little benzene, m. 57-9° (57.5°). The analysis was satisfactory (found, C, 71.8 ; H, 5.9 %, calculated for $C_{14}H_{16}O_4$: C, 71.8 ; H, 5.6 %).

6.4.2 : Allyl benzoate (XIII).

The ester was prepared by simple benzoylation of allyl alcohol, b. 78-80°/ 2 mm. (80°/ 1mm.).

6.5.1 : Propylene diacetate (XVI).

Propylene glycol reacted with acetic anhydride (with considerable violence) over zinc chloride. The main fraction corresponded to the desired product, b. 188-91°/ 760 mm. (b. 191°/ 760 mm., and the analysis was satisfactory (found, C, 52.4 ; H, 7.8 %, calculated for $C_7H_{12}O_4$: C, 52.5 ; H, 7.6 %).

6.5.2 : Propylene dibenzoate (XVII).

The ester was prepared by simple benzoylation of

propylene glycol (using 20 % excess benzoyl chloride), b. 202-3°/ 4 mm. (b. 232°/ 12 mm.).

6.6 : Compounds obtained from external sources.

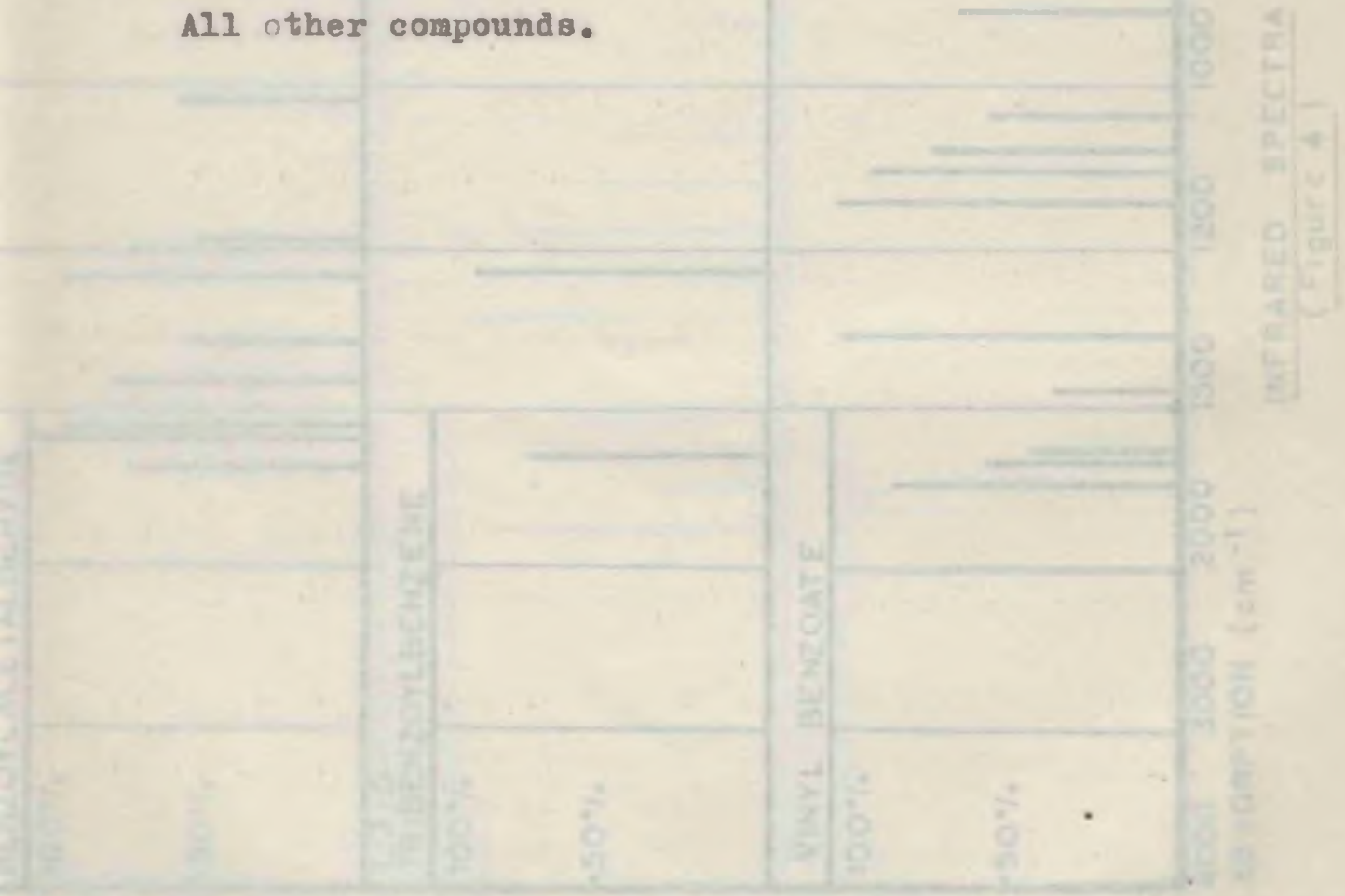
1) By gift.

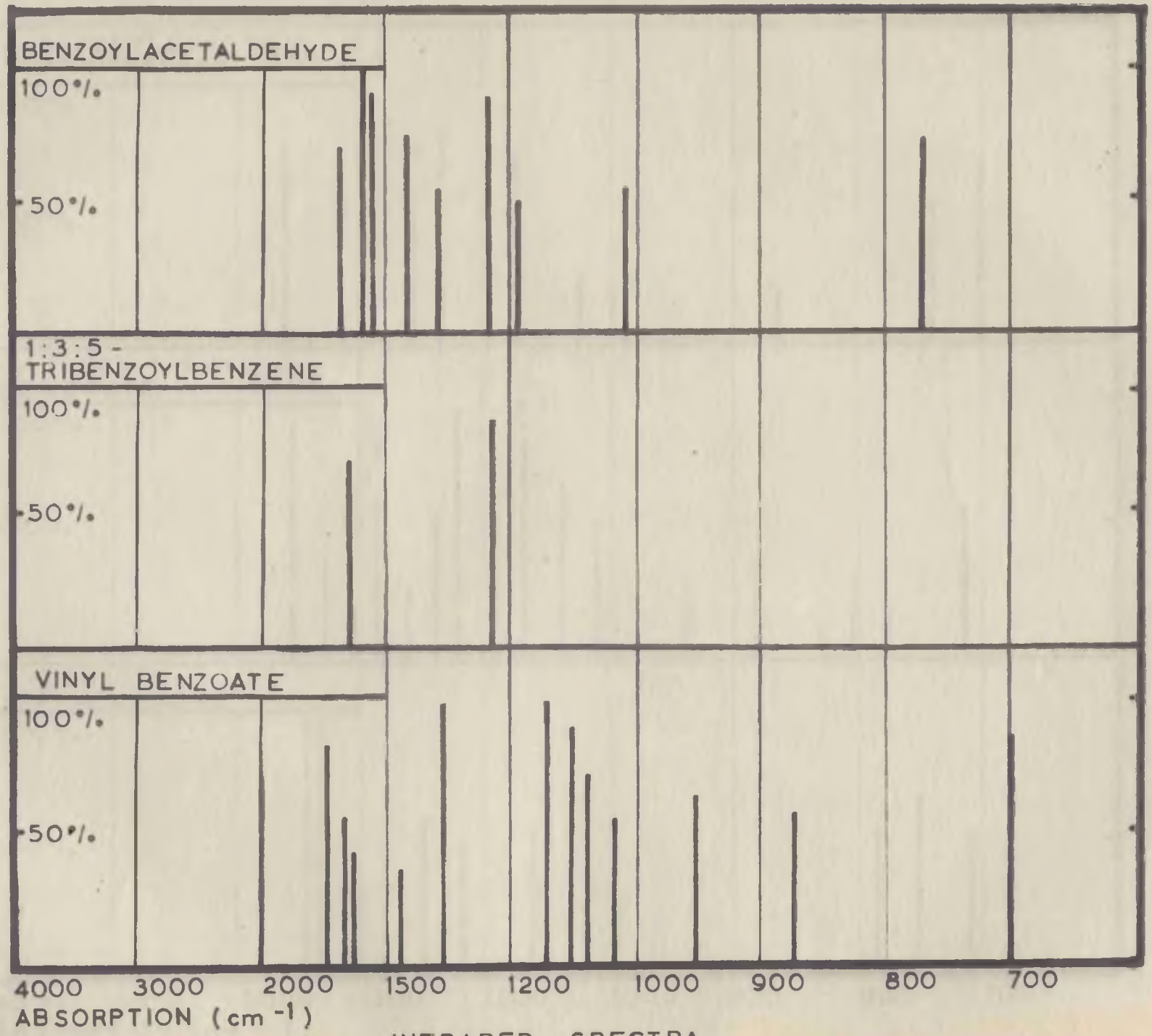
2-Benzoyloxyethyl terephthalate (97), additional to 6.2.1.

Methyl terephthalate (i.e., dimethyl terephthalate) (97).

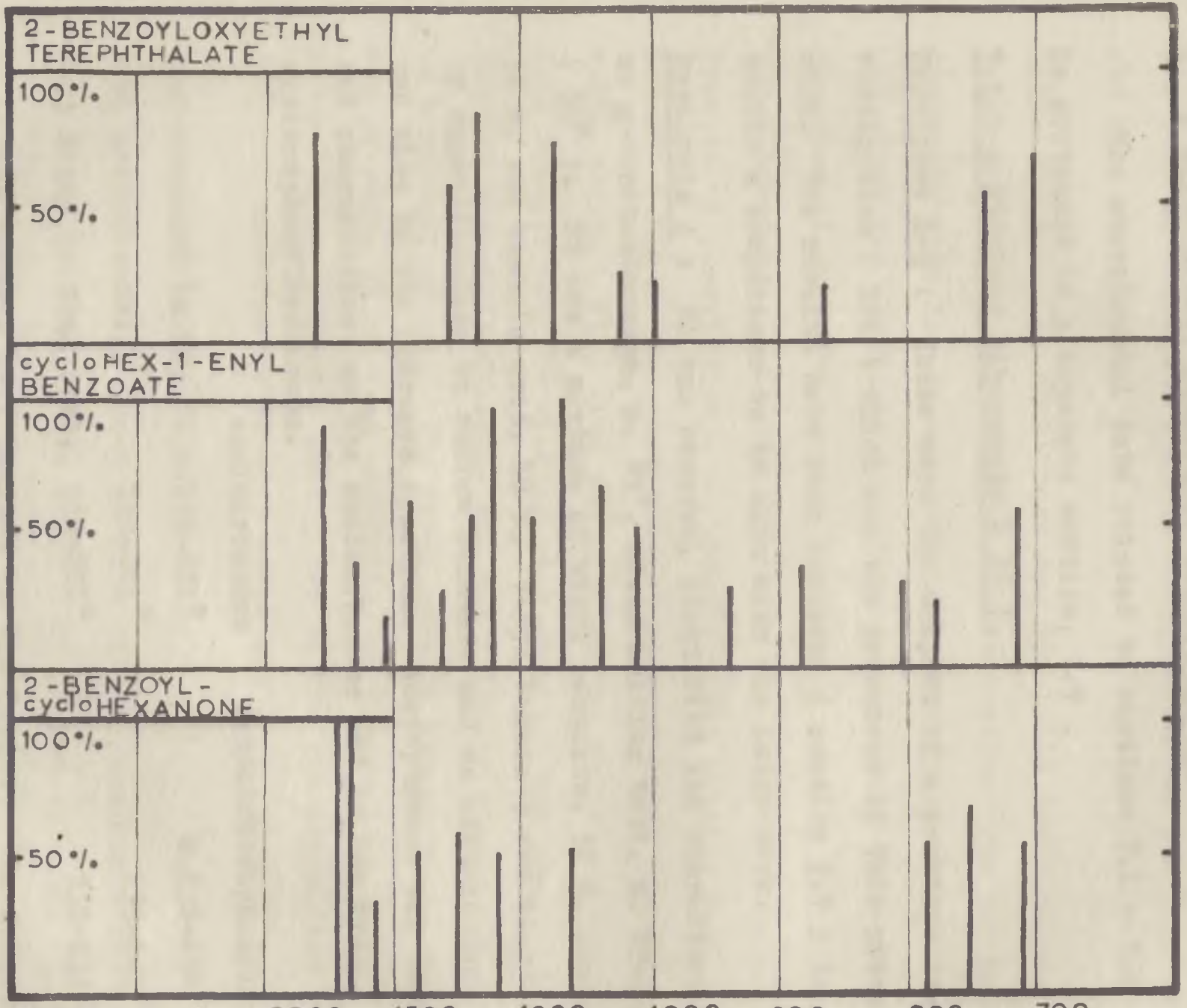
2) By purchase.

All other compounds.





INFRARED SPECTRA
(Figure 4)



INFRARED SPECTRA

(Figure 5)

The Pyrolysis of Model Compounds.

7 : Experimental Results of the Pyrolyses.

The experimental data related to sections 7.1 - 7.6 is contained in a separate section, 7.7 .

7.1.1 : Ethylene dibenzoate (II).

Pyrolyses 1-3 : These were the subject of a previous investigation (104) which was the precursor of this present work. The results have been included (section 7.7) to enable a comparison to be made with the later work.

Pyrolysis 4 : F1 was benzene, identified and characterised as m-dinitrobenzene, m. 89°, mixed melting test, m. 89-90° (90°). F2 was a mixture of vinyl benzoate, 52 %, acetophenone, 38 %, and benzoic acid, 10 %. Vinyl benzoate was identified by saponification to sodium benzoate and an acetaldehyde resin, and also by the infrared spectrum. Acetophenone was identified and characterised as the semicarbazone and as the 2:4-dinitrophenylhydrazone.

	semicarbazone	2:4-dinitrophenylhydrazone
a) Compound in F2,	m.199-201°	m.236-238°
b) Acetophenone,	199-201°	239-242°
c) Mixed melting test,	199-201°	232-234°

The benzoic acid present in the fraction was determined by titration with standard alkali, and the acetophenone was

determined by the method of Iddles et al. (105). The benzoic acid was identified by mixed melting test, m. 119-121° (121°). The residue contained benzoic acid, unchanged ethylene dibenzoate, and charred residue.

Pyrolysis 5 : The pyrolysand was specially purified and recrystallised from benzene. The exit-gases from the Drikold condenser were led to a 2:4-dinitrophenylhydrazine gas trap, and after the pryolysis the Drikold condensate was allowed to vaporise at room temperature, producing a heavy precipitate in the reagent-trap. This precipitate was identified as the derivative of acetaldehyde, m. 157-9°, mixed melting test, m. 158-60° (161-2°). Distillation removed vinyl benzoate and acetophenone (F1) from the pyrolysate, which was then freed from benzoic acid by washing with alkali. The residue was extracted with cold ethanol, and the filtrate evaporated (cold) in a current of air. The final residue became blue, indicating the presence of an acid anhydride, on treatment with (p-nitrobenzamido)phenylacetic acid (106), and was identified by its infrared spectrum as benzoic anhydride (ca. 10 % of residue).

7.1.2 : Benzoylacetaldehyde (IV).

Pyrolysis 6 : The greatest part of the pyrolysate distilled over a narrow temperature range (F2), and this was found to be acetophenone (as also F1) by examination of its infrared spectrum. The semicarbazone was also prepared, m. 199-201°,

and this was confirmed as being the derivative of acetophenone by mixed melting test. The residue consisted of charred and resinous material, and there was no evidence for the presence of any unchanged ketoaldehyde.

Pyrolysis 7 : The first two fractions (F1,F2) were acetophenone (confirmed by infrared), but the third (F3) was found to consist of unchanged ketoaldehyde and a little acetophenone. There was, however, considerably more residue in this pyrolysis than in the last, this time mainly in the form of a brown resin. Further investigation has shown that benzoylacetaldehyde can be distilled (b. 94-8°/ 1 mm., vide section 6.1.2), but not without ca. 33 % resinification. Hence, a fair amount of this pyrolysate residue may have been produced on distillation rather than during the high temperature pyrolysis itself.

The carbon dioxide detected in both pyrolyses (6 and 7) is presumed to be the product of a minor side-reaction, which most likely is related to the known impurity (1:3:5-tribenzoylbenzene) and not the ketoaldehyde itself.

7.1.3 : Vinyl benzoate (III).

Pyrolysis 8 : The first fraction was identified as benzene by boiling point, and also the initial amount of the next fraction (F2). The next two fractions (F 2-3) were a mixture of unchanged vinyl benzoate and acetophenone. The latter was

identified as the semicarbazone, and was present in F2 to the extent of 80% . The total acetophenone content in the pyrolysate was 32 %, and hence the acetophenone produced on pyrolysis was ca. 26 % (allowing for original content of the pyrolysand). The last fraction was identified as benzoic acid, and the residue consisted of the usual tars.

The gas pyrolysate contained acetylene (identified by the infrared spectrum and as the red copper acetylide), but no trace of keten (by aniline test) or divinyl ether could be found. There was no evidence for the presence of these last two gases in the infrared spectrum.

Pyrolyses 9-12 : These four pyrolyses were carried out over the temperature range 300-500°, to determine the effect of temperature on the rearrangement reaction of vinyl benzoate. In each case, the actual amount of acetophenone produced pyrolytically was estimated, and this was found to increase with temperature. These results are shown below, along with the corresponding results of pyrolyses 8 and 13.

Pyrolysis,	9	10	11	12	13	8
Feed rate (g./min.)	0.25	0.27	0.30	0.30	0.27	0.40
Temperature, °C	300	350	400	500	500	550
Acetophenone, %	8.0	10.5	16.5	21.8	19.0	26.0
Reactor,	3	3	3	3	3	2

These results have been plotted, and it has been found that over this range an approximately linear reaction exists. This may be expressed by the following equation, where T = temper-

ature, and a = acetophenone content:

$$T = 14.2a + 190$$

This relationship is only approximate, however, in view of the existing experimental variations.

The pyrolysate of number 12 was fractionated, but did not differ in analysis from that of pyrolysis 8.

Pyrolysis 13 : In this pyrolysis the first two fractions (F1,F2) were examined much more critically, and it was found that the infrared spectrum of F1 showed considerable amounts of an unidentified compound. This was thought to be styrene, and further infrared examination confirmed this. Subsequently, further traces of styrene have been identified in F2 and F3. Otherwise, these fractions contained unchanged vinyl benzoate and acetophenone. There was no trace in any of these fractions of benzaldehyde, and F4 contained benzoic acid. An estimation of total acidity was carried out, and this was calculated as 8 % benzoic acid.

The gas pyrolysate was examined by infrared, and found to contain ethylene, acetylene, and traces of methane. There was no indication of the presence of divinyl ether, but the spectrum contained an unidentified band at 1140 cm^{-1}. The aniline test for keten was again negative.

Pyrolysis 14 : This pyrolysis was carried out in a Pyrex reactor packed with freshly prepared stainless steel turnings

to determine the effect of this material on the direction of pyrolysis. The production of substantial amounts of hydrogen and paraffin gases has been notable, together with a reduction in the amount of unsaturated hydrocarbon gases produced. The relative amounts of hydrogen and paraffin (ratio, 1.81) compares favourably with the amounts of these gases produced on the pyrolysis of ethylene (pyrolysis 43) under equivalent conditions (ratio, 1.97). Tests carried out in the course of pyrolysis for the presence of keten and any other volatile carbonyl compound were both negative. It was noted that a considerable amount of carbon had been deposited on the stainless steel. Fractions 1 and 2 were examined by infrared analysis, and F1 was found to contain a fair amount of styrene, together with vinyl benzoate and acetophenone. F2 however contained only vinyl benzoate and acetophenone, and F3 was benzoic acid.

Pyrolysis 15 : Equimolar quantities (= 0.15 moles) of vinyl benzoate (22 g.) and benzoic acid (18 g.) were co-pyrolysed in this reaction to discover whether any reaction took place between these two compounds in the course of the pyrolysis. It was found that a substantial amount of a 2:4-dinitrophenylhydrazone was produced on passing the gas pyrolysate through the reagent-trap, and this was identified as the derivative of acetaldehyde. The main pyrolysate was not fractionated, but was examined for the presence of benzoic anhydride, which was confirmed by the colour test. By way of

comparison, some pure benzoic acid was pyrolysed (pyrolysis 44) under equivalent conditions, and it was found that the pyrolysate gave a very much paler blue colour than the above pyrolysate. It has therefore been assumed that the copyrolysis had been responsible for the production of acetaldehyde and benzoic anhydride, and that neither pyrolysand alone was capable of yielding these products in such quantity, if at all. It was estimated that 0.0023 moles of acetaldehyde were produced, and that there had been a conversion of ca. 1.5 %. It is possible, however, that the true conversion was somewhat higher than this (because of known difficulties in this estimation when carried out in the course of a pyrolysis). The gas analysis differs little from that reported of the pyrolysis of vinyl benzoate alone, which is not surprising in view of the thermal stability of benzoic acid. It is, however, clear that the two pyrolysands do react together, and that this reaction is very probably also encountered where these two compounds are themselves produced by a primary scission, as, e.g., in the pyrolysis of ethylene dibenzoate.

To provide additional information on this point, several supplementary reactions have been carried out, and these are reviewed below.

(15a) Equimolar quantities of vinyl benzoate and benzoic acid were refluxed for 4 hours at 260-300° in the absence of any catalyst, yielding (almost quantitatively) acetaldehyde

and benzoic anhydride, the latter being in sufficient quantity for redistillation and complete identification (m. 35°, mixed melting test, m. 39-41°, literature quotes 42°).

(15b) Equimolar quantities of vinyl acetate and acetic acid could be made to undergo an equivalent reaction only in the presence of a mercuric catalyst (acetate and sulphate). While only a faint anhydride test could be obtained from this reaction mixture, a ca. 20 % yield of ethylidene diacetate (identified by infrared spectrum) was recorded. The full significance of this result has been discussed in section 3.1.3.

(15c) A similar reaction in the absence of any catalyst has been observed on refluxing cyclohex-1-enyl benzoate with an equimolar quantity of benzoic acid. A small amount of cyclohexanone was identified by infrared analysis, and benzoic anhydride was identified by the colour test reagent and by infrared analysis.

7.2.1 : 2-Benzoyloxyethyl terephthalate (VII).

Pyrolysis 16 : This pyrolysis served as a preliminary investigation, using all the material then available. The total pyrolysate was examined by infrared analysis, and was found to contain vinyl benzoate. This pyrolysate was then taken up in ether and the insoluble residue washed with dilute sodium bicarbonate solution. This extract on acidification yielded

benzoic acid and terephthalic acid.

Pyrolysis 17 : Of the pyrolysate, 2g. were collected in the Drikold condenser. This condensate did not contain any keten (aniline test) but gave the 2:4-dinitrophenylhydrazone of acetaldehyde. The total pyrolysate was taken up in ether, and the insoluble residue removed. As in the previous pyrolysis, the residue contained terephthalic acid, together with unchanged ester. The acidified extract did not yield benzoic acid, probably because the ether extraction was more efficient. However the ethereal solution yielded 12 g. benzoic acid on alkaline washing, although no trace could be found of 4-acetylbenzoic acid in this fraction. The remaining ethereal solution was then distilled, after removal of the ether, and the infrared spectrum of F1 showed it to be a mixture of vinyl benzoate and acetophenone. Traces of this fraction continued into F2, which also contained benzoic acid. No other products were identified, and all attempts to isolate 4-acetylbenzoic acid were fruitless. Much carbonisation occurred during the pyrolysis.

Pyrolysis 18 : The ester for this pyrolysis was recrystallised from ethanol, as in the two previous pyrolyses, but was supplied by an external source (97). There was so much carbonisation that a second reaction tube had to be substituted after about half the material had been pyrolysed. This carbonisation

blocked the system, as evidenced by an increase in pressure. The Drikold condenser yielded 3 g. of liquid, n_D^{20}, 1.492 (benzene, n_D^{20}, 1.506), and this yielded m-dinitrobenzene. It is clear that this is the product of decarboxylation of benzoic acid, and purely visual evidence for the presence of benzene has been found in most of the pyrolyses of benzoates where a sufficient quantity has been pyrolysed. Acetaldehyde was also present in this pyrolysate (cf. pyrolysis 17). The main pyrolysate (58 g.) gave a distillate of 25 g., of which the fractions 1-3 were strictly comparable to the fractions 1-2 of pyrolysis 17. A detailed analysis of F3 failed to reveal any carbonyl compound, other than faint traces of acetophenone. This analysis was carried out by attempting to prepare the 2:4-dinitrophenylhydrazone and by the infrared spectrum. The residue from distillation contained unchanged ester and terephthalic acid, and from an ethereal extract it was possible to isolate and purify ethylene dibenzoate. This was recrystallised from ethanol, and confirmed by a mixed melting point test.

Pyrolysis 19 : The ester for this pyrolysis was from the same source as the previous pyrolysis, but in this case it was recrystallised from benzene. This course was adopted in order to demonstrate that the acetaldehyde previously found was a genuine product, and not from residual traces of the solvent of recrystallisation. The pyrolysis also took place at a lower

temperature (400°) in an attempt to make the conditions more favourable for the isolation of 4-acetylbenzoic acid. Of the pyrolysate, 1 g. was collected in the Drikold condenser, and this consisted mainly of acetaldehyde. The 2:4-dinitrophenylhydrazone was prepared, and confirmed by the mixed melting point test. It was thus clear that acetaldehyde was a genuine product of the pyrolysis. From the main bulk of the pyrolysate, 39 g., there was distilled ca. 1 g. of vinyl benzoate and acetophenone (F1), and a very small amount of benzoic acid (F2). The residue, ca. 38 g., was taken up in cold ether and washed with dilute potassium carbonate solution. The whole mixture was filtered, and thereafter the two layers were separated. Thus, three fractions were isolated:

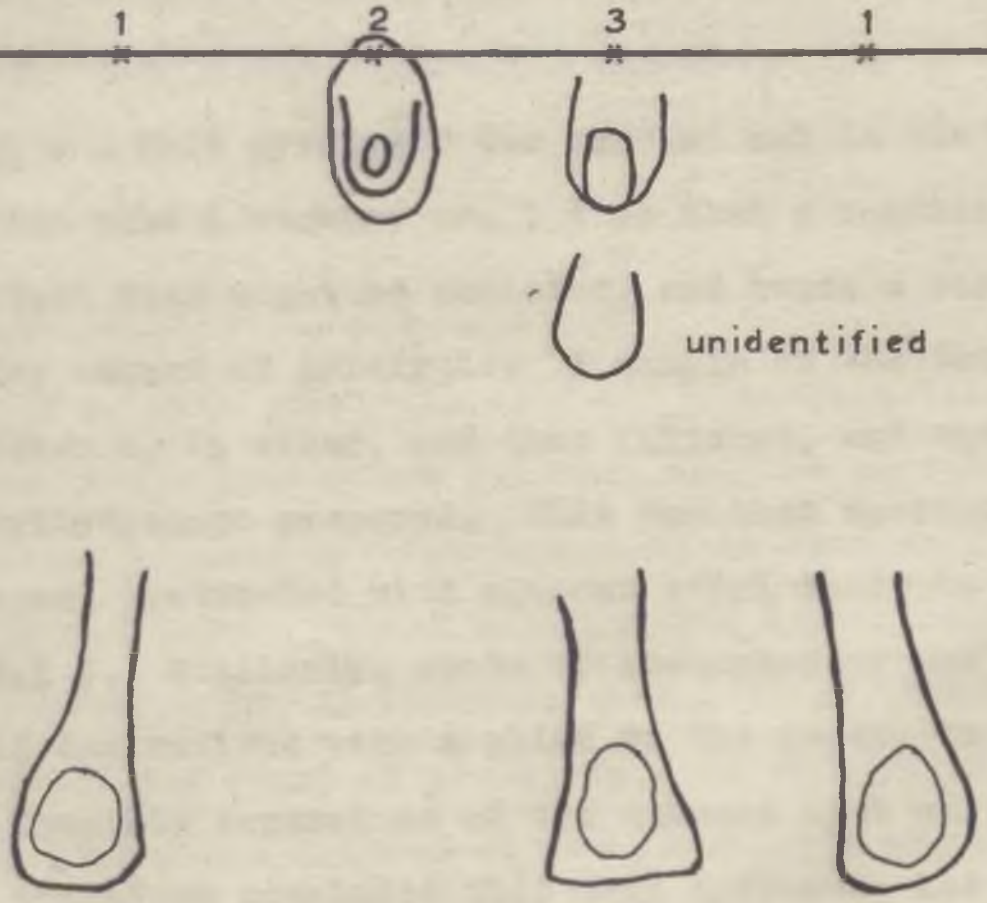
(a) total insoluble, 14 g., consisting of unchanged ester and a small amount of potassium terephthalate,

(b) aqueous solution of potassium benzoate and potassium terephthalate, yielding 14 g. of benzoic acid and 1 g. of terephthalic acid, and

(c) Ethereal solution which yielded 9 g. of residue, solid.

The third fraction (c) yielded crystals of ethylene dibenzoate (cf. pyrolysis 18) and the residue from this was found to contain benzoic anhydride. The latter was identified by the colour test reagent, which gave a very strongly positive reaction. A careful search was made in all three fractions for evidence of the presence of any carbonyl compounds, but,

1) ACETOPHENONE
2) 4 - ACETYLBENZOIC ACID
3) FRACTION from PYROLYSIS 21



CHROMATOGRAPHIC SEPARATION OF
2:4 - DINITROPHENYLHYDRAZONES (Figure 6)

apart from traces of acetophenone, nothing could be found which corresponded to 4-acetylbenzoic acid.

Pyrolysis 20 : The total pyrolysate from this run was taken up in ethanol, and the 2:4-dinitrophenylhydrazone prepared. This was submitted to paper chromatography, using standard methods. These were unsuccessful, and it was clear that the method required considerable research to make it suitable for the mixtures involved.

Pyrolysis 21 : This pyrolysis was carried out in the very large reaction tube (reactor no. 1) so that a considerably greater contact time might be achieved, and hence a correspondingly greater amount of pyrolysis. A sample of the total pyrolysate was taken up in ether, and then filtered, and the 2:4-dinitrophenylhydrazone prepared. This was then spotted on standard paper, pretreated with aqueous ethyl tartrate (vide section 7.8.1). Similarly, spots of acetophenone and 4-acetylbenzoic acid derivatives were applied to the paper, to act as controls. Complete separation of the unknown spot was observed, and it was therefrom concluded that this hydrazone had been a mixture of those of acetophenone and 4-acetylbenzoic acid. These results are summarised below (vide Figure 6).

Run	Eluent	Separated: Acetophenone	4-Acetylbenzoic acid	Unidentified
1	2% CCl_4 in 60/80 petrm.	definite	probable	
2	20% acetone in 60/80 petrm.	"	definite	spot, midway, ?
3	"	"	"	"

These results show that this separation is reproducible, and the identification is thus complete. The third spot observed was extremely faint, and as yet has not been identified, but probably corresponds to one of the several possibilities enumerated in section 3.2.1.

7.2.2 : 4-Acetylbenzoic acid (VIII).

Pyrolysis 22 : This pyrolysis of 4-acetylbenzoic acid was carried out in the semi-micro reactor, and the reaction tube was basically the same as that described in section 5.2, except that it did not have a packed bulb in zone II. Pyrolysis was allowed to proceed for 10 minutes, zone I being covered immediately at the start of pyrolysis. At the end of the pyrolysis, zone I was allowed to return to room temperature, whereupon 40 ml. of gas were transferred to the reservoir. The gas was analysed by Sleigh's method (107), and the total amount of carbon dioxide produced was calculated to be 13.0 ml. Since complete decarboxylation would have produced 137 ml. of carbon dioxide, it was calculated that decarboxylation had occurred to the extent of 9.5 %, which is therefore an

accurate measure of the stability of 4-acetylbenzoic acid under the conditions used.

Pyrolysis 23 : The reaction tube used in this pyrolysis was that described in section 5.2, and in this case the first furnace was advanced slowly over zone I, the operation taking 3 minutes to complete. Pyrolysis by reflux then proceeded for a further 7 minutes at the end of which zone I was uncovered. In this pyrolysis the quantity used was considerably less than in pyrolysis 22, as this was found to be nearer the optimum quantity for the apparatus. The gas evolved by pyrolysis was 9 ml., while the total gas collected in the reservoir was 30 ml. From the Sleigh analysis, 10.5 ml. of carbon dioxide were produced, and hence 25.6 % decomposition by decarboxylation had taken place. The presence of acetophenone in the pyrolysate was indicated by smell, and also by the sodium nitroprusside test for methyl ketones (vide section 7.8.2), which showed a distinct difference when applied to pyrolysand and pyrolysate respectively. The colour difference in the test was equivalent to that produced by acetophenone.

7.3.1 : cycloHex-1-enyl benzoate (IX).

Pyrolysis 24 : This first exploratory pyrolysis was essentially for the purpose of discovering whether thermal rearrangement of the enol ester took place. The total liquid pyrolysate did not crystallise on standing over a short period (several

days), but a small sample was seen to have crystallised into long needles after the passage of several months. However, after the pyrolysate had been fractionated, the third fraction crystallised overnight, and corresponded exactly with the expected product of rearrangement, 2-benzoylcyclohexanone. This was confirmed by mixed melting test with a small sample prepared by synthesis (reaction of cyclohexanone with phenyl benzoate in the presence of sodamide, 108). The crystals from F3 melted at 89-91°, and crystals from synthesis (very small quantity, precluding proper recrystallisation) melted at 82-84°, mixed melting test, m. 84-86° (89-91°). Microcombustion found C, 77.4 ; H, 7.13 % (calculated for $C_{13}H_{14}O_2$: C, 77.3 ; H, 6.94 %). The infrared spectrum of the two isomers agreed with the theoretical requirements of the respective functional groups. The second fraction was mainly unchanged ester, but after a short time (2 weeks), some more of the isomeric diketone crystallised out. In view of the closeness of the boiling points of the two isomers, it is doubtful whether a complete separation by distillation could be effected. The first fraction was found to contain cyclohexanone, which was identified as the 2:4-dinitrophenylhydrazone, m. 152-5°, mixed melting test, m. 154-7° (162°).

Pyrolysis 25 : This pyrolysis was carried out to provide confirmation of the results of pyrolysis 24. The surprising

discovery of cyclohexanone in F1 was confirmed, and it was also shown that it was a genuine product of pyrolysis, being absent from the original pyrolysand. Fractions 2 and 3 were strictly comparable to those of pyrolysis 24, and all the 2-benzoylcyclohexanone so obtained was utilised in later pyrolyses. The combined pyrolysate residues of 24 and 25 were submitted to pyrolysis several times, the content of 2-benzoylcyclohexanone being removed by distillation after each pyrolysis. It was thus possible to gain sufficient of the isomeric diketone for further study. In the course of this it was noticed that a small amount of benzoic acid had accumulated, and it was realised that this was a minor product which had only been revealed by the process of repeated pyrolysis. The 2-benzoylcyclohexanone thus prepared was recrystallised from ethanol, m. 89-90°, and in all 14 g. were obtained.

Pyrolysis 26 : This third pyrolysis was carried out in the semi-micro unit under the static conditions obtained by allowing the pyrolysate to reflux back into zone II. The first furnace was introduced over zone I over a period of 5 minutes, and pyrolysis continued thereafter for a further 5 minutes. The gas evolved by pyrolysis was 8 ml., and altogether 27 ml. were collected in the reservoir. Apart from the gas analysis, practically no further information was obtained from this

pyrolysis, except that the test for the presence of an acid anhydride was negative.

7.3.2 : 2-Benzoylcyclohexanone (X).

Pyrolysis 27 : This pyrolysis was carried out on material obtained by the repeated pyrolysis of cyclohex-1-enyl benzoate (vide pyrolyses 24 and 25), and the material was recrystallised from ethanol, m. 89-90° (89-91°). The liquid pyrolysate was initially subjected to atmospheric distillation, yielding a small fraction (F1). This fraction gave a 2:4-dinitrophenylhydrazone, which was identified as that of cyclohexanone. The remainder of this fraction was analysed by infrared, the spectrum being found to represent mainly cyclohexanone, together with several fairly strong impurity bands. These bands corresponded exactly with the spectrum of benzene, and another single band (1265 $cm.^{-1}$) suggested the presence of cyclohex-1-enyl benzoate. The residue from this distillation was tested for the presence of anhydride, but the result was negative. Thereafter, distillation at reduced pressure yielded a further two fractions (F2 and F3). The second fraction remained completely liquid for 4 days, after which a few crystals appeared (unchanged diketone). The supernatant liquid was analysed by infrared, and was clearly identified as cyclohex-1-enyl benzoate, together with evidence of dissolved diketone. The third fraction gradually crystallised, and only

a very small amount of filtrate (corresponding with F2) was left. This last fraction was also unchanged diketone.

Pyrolysis 28 : This pyrolysis was carried out in the semi-micro unit, the first furnace being introduced over zone I over a period of 5 minutes. The results of this run are quite out of keeping with all the others of the two isomers (pyrolyses 24-26, and 27-30), and it is now felt that they are not reliable. Apart from charring, very little pyrolysis appeared to have occurred, the pyrolysate crystallising within a few hours of cooling. It is probable that the furnace suffered heat losses during the second period of 5 minutes when pyrolysis was allowed to continue by reflux. The pyrolysis evolved 12 ml. of gas, and altogether 33 ml. were collected in the reservoir.

Pyrolysis 29 : This was a repeat of pyrolysis 28, using in this case the optimum quantity of pyrolysand for the apparatus. The sequence of operations of pyrolysis was the same as that for 28, and pyrolysis evolved 22 ml. of gas, and 42 ml. were collected in the reservoir. A small fraction (ca. 50 mg.) distilled out of the reflux into the second bend, and this was collected, and analysed by infrared. The spectrum corresponded mainly to cyclohexanone, and it was also possible to identify positively cyclohex-1-enyl benzoate. The main pyrolysate was very charred, and no further analysis was attempted. It did not crystallise within 2 weeks, and was not observed beyond

that period.

Pyrolysis 30 : This pyrolysis was carried out to complete the study of the gas pyrolysates of the two isomers. The first furnace was introduced over zone I over a period of 5 minutes. The reaction tube was in the inverted position (giving straight-through flow and no reflux) and pyrolysis was complete in ca. 30 seconds. The gas evolved by pyrolysis was 4 ml., this taking place over 20 seconds, and the total gas collected in the reservoir was 28 ml. The pyrolysate was only slightly charred, and crystallised almost immediately.

Pyrolyses 24-30 : The Relative Compositions of Gas Pyrolysates.

It was noticed that the relative proportions of carbon monoxide and carbon dioxide varied very considerably throughout the pyrolyses of cyclohex-1-enyl benzoate and 2-benzoylcyclohexanone. To provide a measure of comparison, therefore, the percentage ratio CO_2/CO has been compared with the degree of pyrolysis, as indicated by the ratio of gas produced per unit weight of pyrolysand. These figures are given below.

Pyrolysis of cycloHex-1-enyl benzoate.

Pyrolysis,	26	24	25
Gas prod./pyrolysand, i.e., ml./g.	6.8	37.5	50
Ratio CO_2/CO,	0.31	0.14	0.07

Pyrolysis of 2-Benzoylcyclohexanone.

Pyrolysis,	30	27	29	(28)
Gas prod./pyrolysand, i.e., ml./g.	13.3	35.7	73	12
Ratio CO_2/CO,	0.36	0.32	0.87	3.7

The significance of these results has been discussed in section 3.3.2.

7.3.3 : Acetylacetone (XI).

Pyrolysis 31 : This pyrolysis was carried out mainly to discover the quantities of carbon monoxide and carbon dioxide produced on pyrolysis of a β-diketone. This percentage ratio (CO/CO_2) was found to be 4.5. The liquid pyrolysate was fractionated, and the refractive indices of these fractions proved to be of interest.

n_D^{20}: F1, 1.385 ; F2, 1.419 ; F3, 1.448.

The refractive index of F1 could indicate the presence of acetone (1.390_0), while F3 is clearly unchanged acetylacetone (1.451_5 , b. 136° / 760 mm.). F1 was not analysed further (because of the quantity), but infrared analysis of F2 indicated that this fraction was mainly acetylacetone. The spectrum, however, contained strong evidence for the presence of isopropenyl acetate. This peint was not further studied, however.

7.4.1 : Trimethylene dibenzoate (XII).

Pyrolysis 32 : The exit-gases were passed through a 2:4-dinitrophenylhydrazone trap before being collected in the reservoir, and a precipitate was produced. This could not be recrystallised from ethanol, and only from glacial acetic acid, m. 162-4°, which suggested that the original compound was acrolein (derivative, m. 168°). A mixed melting test with the derivatives of acetaldehyde and propionaldehyde respectively showed considerable depression of the melting point, whereas this did not occur with the derivative of acrolein (m. 164-5°). The contents of the Drikold trap also produced this derivative, again indicating the presence of acrolein. The main pyrolysate was fractionally distilled under reduced pressure into 4 fractions. Of these, F1 contained traces of acrolein, and boiled at 160° (by capillary tube test). It was thus clear that the main fraction was not acrolein, and the infrared spectrum was therefore taken. This spectrum contained bands which might have been assigned to (a) an alcohol, and (b) a vinyl compound. It has not, however, been possible to identify the compound from the above evidence, and its true nature therefore remains obscure. Fractions 2 and 3 may be regarded as equivalent, and the capillary tube test indicated that the

substance boiled at 228-230°. Alkaline hydrolysis yielded benzoic acid and allyl alcohol, the latter being confirmed by preparation of the urethane, m. 65-7° (67°). The substance was therefore identified as allyl benzoate (b. 230°). In the course of alkaline hydrolysis it was observed that there was a small amount of non-saponifiable liquid. This liquid was isolated, and the infrared spectrum taken. This spectrum bore such strong similarities to that of styrene, that it was deduced that the compound was allylbenzene. The latter was synthesised (by a Friedel-Crafts type of reaction between allyl alcohol and benzene in the presence of aluminium chloride, 109), and the spectrum was found to be identical to that of the pyrolysate fraction. The last fraction (F4) was benzoic acid, and a further 20 g. of benzoic acid were washed out of the residue (27 g.). The remaining 7 g., which were very heavily charred, were not further analysed.

Pyrolysis 33 : This differed from pyrolysis 32 in that the pyrolysand was introduced in pellet from by the solenoid feeder device (vide section 5.1). There were 124 pellets, with an average weight of 0.85 g. per pellet, and the pellets were introduced at the rate of one per minute. The pyrolysate was fractionated and was strictly comparable to the fractions obtained in pyrolysis 32. The second fraction was carefully examined for the presence of any carbonyl compound (which

might arise from a B scission of allyl benzoate), but no trace could be found. As before, F2 and F3 were the same, i.e., allyl benzoate and allylbenzene. The residue from distillation (79.5 g., allowing for 2 g. losses) yielded 22 g. of benzoic acid, and a residue of mainly unchanged ester (38.5 g.). This residue gave a strongly positive test for the presence of an acid anhydride. The gas pyrolysate was examined by infrared, and the spectrum showed the presence of ethylene, acetylene, and the possible presence of methane. There were also several unassigned bands, which were attributed to the gaseous pyrolysis products of acrolein (vide pyrolysis 36). No further information about F1 was obtained from this pyrolysis.

7.4.2 : Allyl benzoate (XIII).

Pyrolysis 34 : The infrared spectrum of this gas pyrolysate was almost identical to that obtained in pyrolyses 32 and 33, and this fact was again attributed to the products of pyrolysis of acrolein. The first fraction from distillation of the liquid pyrolysate contained acrolein, which was also found in F2. The third fraction consisted of unchanged allyl benzoate, and no intermediate fraction could be found which might have contained benzaldehyde. It was noticed that very little cracking appeared to have taken place.

Pyrolysis 35 : In view of the surprising inability to

identify benzaldehyde as a product of the pyrolysis of allyl benzoate, this pyrolysand contained an added 5 % of redistilled benzaldehyde. A small amount of liquid (less than 1 g.) was collected in the Drikold trap, and the infrared spectrum indicated that this was the same as the unidentified F1 of pyrolysis 32. The liquid pyrolysate was fractionally distilled, the first fraction containing acrolein, and benzene. The second fraction was mainly allyl benzoate, but the infrared spectrum indicated that benzaldehyde was also there to a very small extent. It was thus clear that it was possible to account for only a small amount of the benzaldehyde added to the pyrolysand, and certainly none of the benzaldehyde produced by pyrolysis. The third fraction consisted of allyl benzoate, and F4 contained a trace of benzoic acid.

7.4.3 : Acrolein (XV).

Pyrolysis 36 : The infrared spectrum of this gas pyrolysate closely corresponded to the spectra of the gas pyrolysates of trimethylene dibenzoate and allyl benzoate. It was therefore concluded that acrolein had been the source of these gases. The liquid pyrolysate was carefully fractionated, but no fraction could be found to correspond to the unidentified fraction in pyrolyses 32 and 35. The second fraction was unchanged acrolein, and in fact so were F1 and F3.

7.4.4 : Benzaldehyde (XIV).

Pyrolysis 37 : In this pyrolysis benzaldehyde was treated under the same conditions as the above esters, and it was found that very little decomposition had taken place. Fraction 1 contained benzene, and F3 contained a trace of benzoic acid. This pyrolysis showed that benzaldehyde *per se* does not pyrolyse to any appreciable extent under these conditions.

7.5.1 : Propylene diacetate (XVI).

Pyrolysis 38 : This pyrolysis was carried out on an impure sample of the ester, which was found to contain a substantial quantity of the glycol. Since propylene glycol and the ester have virtually the same boiling point, it was found that separation by distillation was impossible. Pyrolysis of this mixture was found to yield considerable quantities of propionaldehyde (identified as the 2:4-dinitrophenylhydrazone), which formed the greater part of F1. The second fraction consisted of allyl acetate, which was hydrolysed to acetic acid and allyl alcohol (identified as the urethane), and F3 contained acetic acid. The last fraction was unchanged ester, and neither this fraction nor F3 contained any anhydride (colour test reaction). Fractions 2-4 were confirmed by infrared analysis.

Pyrolysis 39 : This pyrolysand was a rigorously pure sample,

and its purity was substantiated by a satisfactory microcombustion analysis (vide section 6.5.1). All the exit-gases were passed straight into a 2:4-dinitrophenylhydrazone trap without first going through a Drikold trap. This precipitate was analysed by the special paper chromatrography technique (vide section 7.8.1), which indicated that the carbonyl compound present was almost entirely acrolein, with only a very slight trace of propionaldehyde. The liquid pyrolysate was fractionally distilled, and F1 contained acrolein together with traces of allyl acetate, and F3 and F4 were acetic acid. The last three fractions were combined, washed free of acid and redistilled; a fraction with a narrow boiling range (b. 100-4° / 760 mm.) was collected. This fraction (3 g.) was analysed by infrared, whence it was deduced that it consisted of pure allyl acetate. No indication whatever of the presence of any of the possible isomers of allyl acetate could be found either by infrared or by analysing the products of acid hydrolysis.

7.5.2 : Propylene dibenzoate (XVII).

Pyrolysis 40 : This pyrolysis was carried out to confirm the findings of pyrolyses 38 and 39. The liquid pyrolysate was fractionally distilled, and both F1 and a trace of liquid in the Drikold trap were found to be acrolein. Fractions 2 and 3 were found by infrared analysis to be allyl benzoate, and it

was also clear that none of the possible isomers were present. The benzoic acid produced (31 g.) was removed by washing, and F4 and F5 consisted mainly of unchanged ester. A sub-fraction of F2 (b. 34-48° / 0.7 mm.) contained allylbenzene (identified by infrared analysis).

7.5.3 : Allyl acetate (XVIII).

Pyrolysis 41 : 10 g. of this liquid pyrolysate were collected in the Drikold receiver. It was stable at -60°, but immediately it was removed from the condenser it started to boil vigorously. The gas was bubbled through an aniline trap to test for keten, but this test was negative. The infrared spectrum was then taken, and this showed the presence of a considerable amount of butene-1. The rest of the spectrum bore similarities with the spectra of the gas pyrolysates of allied compounds. It was also possible to prepare a 2:4-dinitrophenyl-hydrazone from the gas, and this derivative was that of acrolein. The remainder of the Drikold condensate was distilled and found to contain acrolein and allyl acetate. These were fractions 1 and 2. The main bulk of the liquid pyrolysate (40.5 g.) was then distilled and the first fraction of this (F3) carefully examined for the presence of an alcohol. This was tested for by the alkali-alkyl xanthate test (vide section 7.8.3), and blanks were prepared using pure allyl alcohol, and also the original ester. The test was negative, and so it was concluded that no alcohol was present. Fractions 4 and 5 were

unchanged ester, and F5 did not give any reaction with the anhydride colour test reagent.

Pyrolysis 42 : This was a repeat pyrolysis of 41, to enable the gas pyrolysate to be investigated fully. Part of the gas was collected separately and then passed through a solution of bromine in chloroform. This was done several times, and then the infrared spectrum of the gas was taken. This showed considerably less absorption than in the previous analysis (pyrolysis 41), and the missing components corresponded to the absorption of butene-1. Other gases present included methane and ethylene. A second part of the gas was passed through the 2:4-dinitrophenylhydrazone trap alone (by-passing the Drikold trap), and this precipitate was carefully analysed by fractional crystallisation. Only the derivative of acrolein, however, could be identified, and it was therefore concluded that acetaldehyde was absent. The liquid pyrolysate did not undergo any further analysis.

7.6.1 : Ethylene (V).

Pyrolysis 43 : The pyrolysand was prepared by the action of concentrated sulphuric acid on ethanol, and then washed with concentrated potassium hydroxide solution, pyrogallol solution, and finally passed through a Drikold trap. At this stage the gas contained 14 % nitrogen. The rate of pyrolysis was equivalent to a flow of 0.005 moles per minute, whereas the

rate of pyrolysis of vinyl benzoate (pyrolysis 14) was 0.002 moles per minute. The reactor was the same as that used in pyrolysis 14, and after pyrolysis, the stainless steel was evenly coated with carbon. The ratio of hydrogen to methane in the gas pyrolysate was 1.97.

7.6.2 : Benzoic acid (XIV).

Pyrolysis 44 : The anhydride colour test was applied to the pyrolysate and pyrolysand respectively, and the results compared. It was found that only the pyrolysate gave a positive reaction, and then only to a small extent. Hence, a very small amount of benzoic acid had been produced on pyrolysis.

7.7 : Tabulated Data related to Sections 7.1 - 7.6.

These data are shown in tables overleaf et seq.

Pyrolyses
7.1.1 : 1-4, Ethylene dibenzoate (II).

Pyr. No.	1	2	3	4
Reactor	6	6	6	2
Temperature	510°	500-510°	400	550
Amt. pyr'd	46 g.	63 g.	50 g.	99 g.
Pyrolysate		31 g.		72 g.
Gas pyr'sate	6·3 l.	15·1 l.	14 l.	7·5 l.
Rate, g./min.	0·75	0·8	0·75	0·4
t_c seconds				16·5
Gas Analysis:				
CO_2	35.9 %	20.2 %	20.0 %	65 %
CO	54·6	45·4	43·6	35
C_nH_{2n}	-	-	-	-
H_2	7·2	26·7	29·8	-
CH_4/C_nH_{2n+2}	2·3	7·7	6·6	-
Pyrolysate Fractions:				
amount				2·5 g.
F1		75-85°/760	Drikold Condensate	46°/180
amount				14·5 g.
F2		ca. 35°/27	75-90°/760	68-106°/24
amount				17 g.
F3		84-96°/19	85-96°/17	124°-/19
amount				38 g.
F4		98-114°/18	120-150°/17	Residue
amount				
F5		120-150°/17		

Pyrolyses

7.1.1 : 5, Ethylene dibenzoate (II).
7.1.2 : 6-7, Benzoylacetaldehyde (IV).
7.1.3 : 8, Vinyl benzoate (III).

Pyr. No.	5	6	7	8
Reactor	3	2	3	2
Temperature	500°	550°	400°	550°
Amt. pyr'd	50 g.	40 g.	40 g.	40 g.
Pyrolysate	46.5 g.	31.5 g.	34 g.	28 g.
Gas pyr'sate	2.5 l.	5 l.	4 l.	8 l.
Rate, g./min.	0.42	0.5	0.33	0.40
t_c seconds	10.0	13.2	14.6	16.5
Gas Analysis:				
CO_2	14.3 %	5 %	2 %	20 %
CO	82.1	95	97	75
C_nH_{2n}	3.5	-	1	5
H_2	-	-	-	-
CH_4/C_nH_{2n+2}	-	-	-	Trace ?
Pyrolysate Fractions:				
amount	12 g.	0.5 g.	0.5 g.	1 g.
F1	60-70°/12	110-115°/55	50-58°/3	26-45°/64
amount	34 g.	27 g.	15 g.	15 g.
F2	Residue	115-116°/55	58-70°/3	96-98°/40
amount		4 g.	6.5 g.	1 g.
F3		Residue	70-108°/3	110-130°/40
amount			12 g.	1 g.
F4			Residue	130°/40
amount				10 g.
F5				Residue

Pyrolyses

7.1.3 : 9-12, Vinyl benzoate (III).

Pyr. No.	9	10	11	12
Reactor	3	3	3	3
Temperature	300°	350°	400°	500°
Amt. pyr'd	40 g.	20 g.	20 g.	30 g.
Pyrolysate	ca. 37 g.	ca. 18 g.	ca. 18 g.	ca. 27 g.
Gas pyr'sate	0·5 l.	0·5 l.	1 l.	2 l.
Rate, g./min.	0·25	0·27	0·3	0·3
t_c seconds	22·8	19·4	16·0	14·0
Gas Analysis:	N_2 : 98 %			
CO_2	-		7·3 %	
CO	2 %		87·8	
C_nH_{2n}	-		4·9	
H_2	-		-	
CH_4/C_nH_{2n+2}	-		-	
Pyrolysate Fractions:				
amount				
F1				62-68°/20
amount				
F2				65-80°/20
amount				
F3				80-128°/20
amount				
F4				
amount				
F5				

Pyrolyses

7.1.3 : 13-14, Vinyl benzoate (III).
7.1.3 : 15, Vinyl benzoate and benzoic acid.
7.2.1 : 16, 2-Benzoyloxyethyl terephthalate (VII).

Pyr. No.	13	14	15	16
Reactor	3	5	3	4
Temperature	500°	500°	500°	ca. 550°
Amt. pyr'd	50 g.	40 g.	40 g.	4 g.
Pyrolysate	40 g.	26·5 g.		3 g.
Gas pyr'sate	6 l.	9 l.	1 l.	ca. 50 ml.
Rate, g./min.	0.27	0.3	0.4	ca. 1
t_c seconds	15·6	23·3	9·6	ca. 9
Gas Analysis:				
CO_2	8.5 %	13.8 %	20.2 %	
CO	73	64·7	69·3	
C_nH_{2n}	18	2·3	10·5	
H_2	-	12·3	-	
CH_4/C_nH_{2n+2}	trace	6·9	-	
Pyrolysate Fractions:				
amount	2 g.	1 g.		
F1	22-64°/4	30-50°/2		
amount	2 g.	15·5 g.		
F2	66-72°/1	50-60°/0·5		
amount	22 g.	1 g.		
F3	72-80°/1	60-100°/1		
amount	10 g.	9 g.		
F4	80°/1	Residue		
amount	4 g.			
F5	Residue			

Pyrolyses

7.2.1 : 17-20, 2-Benzoyloxyethyl terephthalate (VII)

Pyr. No.	17	18	19	20
Reactor	3	2	2	4
Temperature	500°	500°	400°	450°
Amt. pyr'd	66 g.	100 g.	50 g.	10 g.
Pyrolysate	39 g.	61 g.	40 g.	9 g.
Gas pyr'sate	6 l.	12·5 l.	2 l.	
Rate, g./min.	0·54	0·5	0·4	0·3
t_c seconds	24·3	43·5	62·7	ca. 31
Gas Analysis:				
CO_2	22.2 %	42.7 %	43.5 %	
CO	40	53·4	48·7	
C_nH_{2n}	5·6	3·9	7·8	
H_2	5	-	-	
CH_4/C_nH_{2n+2}	27·2	-	-	
Pyrolysate Fractions:				
amount	4 g.	5 g.	1 g.	
F1	70-100°/2	75-86°/4	100-114°/6	
amount	2 g.	4·5 g.	1 g.	
F2	116-160°/1	86-92°/2	114-120°/6	
amount		15 g.		
F3		92-120°/2		
amount				
F4				
amount				
F5				

Pyrolyses

7.2.1 : 21, 2-Benzoyloxyethyl terephthalate (VII
7.2.2 : 22-23, 4-Acetylbenzoic acid (VIII).
7.3.1 : 24, cycloHex-1-enyl benzoate (IX).

Pyr. No.	21	22	23	24
Reactor	1	7	7	3
Temperature	500°	500°	500°	480°
Amt. pyr'd	50 g.	1·000 g.	0·300 g.	40 g.
Pyrolysate	42·5 g.			36 g.
Gas pyr'sate	4·5 l.		9 ml.	1·5 l.
Rate, g./min.	0·7			0·3
t_c seconds	14·7			17·4
Gas Analysis:				
CO_2	40 %	82·4 %	82·4 %	10·8 %
CO	53·3	17·6	17·6	78·4
C_nH_{2n}	6·7	-	-	10·8
H_2	-	-	-	-
CH_4/C_nH_{2n+2}	-	-	-	-
Pyrolysate Fractions:				
amount				5 g.
F1				42-140°/1
amount				18 g.
F2				140-160°/1
amount				5 g.
F3				160-166°/1
amount				4 g.
F4				Residue
amount				
F5				

Pyrolyses

7.3.1 : 25-26, cycloHex-1-enyl benzoate (IX).

7.3.2 : 27-28, 2-Benzoylcyclohexanone (X).

Pyr. No.	25	26	27	28
Reactor	3	7	3	7
Temperature	500°	500°	500°	500°
Amt. pyr'd	40 g.	1·179 g.	14 g.	1·000 g.
Pyrolysate	39 g.		11 g.	
Gas pyr'sate	2 l.	8 ml.	0·5 l.	12 ml.
Rate, g./min.	0·29		0·25	
t_c seconds	19·8		23	
Gas Analysis:				
CO_2	9·4 %	21·7 %	20 %	79 %
CO	85	69·7	62·5	11
C_nH_{2n}	5·6	8·6	17·5	-
H_2	-	-	-	-
CH_4/C_nH_{2n+2}	-	-	-	-
Pyrolysate Fractions:				
amount	3 g.		15 g.	
F1	25-130°/3		40-170°/760	
amount	15.5 g.		1 g.	
F2	130-145°/3		140-148°/1	
amount	12·0 g.		5 g.	
F3	145-168°/3		148-152°/1	
amount	8·5 g.		3·5 g.	
F4	Residue		Residue	
amount				
F5				

Pyrolyses

7.3.2 : 29-30, 2-Benzoylcyclohexanone (X).
7.3.3 : 31, Acetylacetone (XI).
7.4.1 : 32, Trimethylene dibenzoate (XII).

Pyr. No.	29	30	31	32
Reactor	7	7	3	3
Temperature	500°	500°	500°	500°
Amt. pyr'd	0.300 g.	0.300 g.	21 g.	60 g.
Pyrolysate			20 g.	52.5 g.
Gas pyr'sate	22 ml.	4 ml.	ca. 100 ml.	4 l.
Rate, g./min.			0.32	0.5
t_c seconds			5.3	15.6
Gas Analysis:				
CO_2	43.5 %	27.3 %	18.2 %	48.5 %
CO	50.0	62.7	81.8	38.6
C_nH_{2n}	6.5	-	-	12.9
H_2	-	-	-	-
CH_4/C_nH_{2n+2}	-	-	-	-
Pyrolysate Fractions:				
amount			few drops	1.5 g.
F1			65-95°/760	40-70°/7
amount			1 g.	7 g.
F2			100-125°/760	90-98°/6
amount			16 g.	16 g.
F3			128-136°/760	100-109°/6
amount			3 g.	27 g.
F4			136°/760	Residue
amount				
F5				

Pyrolyses

7.4.1: 33, Trimethylene dibenzoate (XII).

7.4.2: 34-35, Allyl benzoate (XIII).

7.4.3: 36, Acrolein (XV).

Pyr. No.	33	34	35	36
Reactor	2	3	3	3
Temperature	400°	455°	500°	480°
Amt. pyr'd	104 g.	50 g.	40 g.	30 g.
Pyrolysate	99·5 g.	59 g.	37 g.	27 g.
Gas pyr'sate	1·5 l.	1 l.	2 l.	3 l.
Rate, g./min.	0·85	0·75	0·33	0·5
t_c seconds	17.5	6.3	13·5	33.6
Gas Analysis:				
CO_2	46·9 %		40·4 %	3·5 %
CO	40.6		47.4	77.5
C_nH_{2n}	12·7		12·2	19·0
H_2	-		-	-
CH_4/C_nH_{2n+2}	-		-	-
Pyrolysate Fractions:				
amount	2 g.	2 drops	1·5 g.	1 g.
F1	50-72°/760	52-120°/760	60-82°/760	20-51°/760
amount	2 g.	1 g.	1·0 g.	25 g.
F2	50-82°/1	40-80°/7	40-80°/10	52-56°/760
amount	20 g.	34 g.	26 g.	1 g.
F3	78-81°/0·5	77-80°/2	80-90°/5	56-58°/760
amount	4 g.	14 g.	1·0 g.	
F4	86°/0·5	Residue	92°/4	
amount	71.5 g.		7.5 g.	
F5	Residue		Residue	

Pyrolyses

7.4.4 : 37, Benzaldehyde (XIV).
7.5.1 : 38-39, Propylene glycol diacetate (XVI).
7.5.2 : 40, Propylene glycol dibenzoate (XVII).

Pyr. No.	37	38	39	40
Reactor	2	3	2	3
Temperature	500°	500°	500°	500°
Amt. pyr'd	50 g.	50 g.	80 g.	79 g.
Pyrolysate	46 g.	40 g.	48 g.	72 g.
Gas pyr'sate	1 l.	5 l.	17 l.	3 l.
Rate, g./min.	0·5	0·56	0·57	0·36
t_c seconds	9·8	8·1	13·2	21·5
Gas Analysis:				
CO_2	-	22·2 %	22·2 %	45·3 %
CO	96 %	35	27	45·7
C_nH_{2n}	4	9·3	17·1	9
H_2	-	-	?	-
CH_4/C_nH_{2n+2}	-	-	present	-
Pyrolysate Fractions:				
amount	1 g.	1 g.	3 g.	1 g.
F1	84-160°/760	50-99°/760	48-105°/760	45-80°/760
amount	41 g.	14·0 g.	13 g.	22 g.
F2	176-180°/760	99-110°/760	105-113°/760	40-90°/0·5
amount	4 g.	15·0 g.	16 g.	3 g.
F3	180°/760	110-130°/760	113-118°/760	82-92°/0 5
amount		8·0 g.	7 g.	1 g.
F4		130-186°/760	ca.118°/760	92-180°/0·5
amount		2 g.	7 g.	6 g.
F5		Residue	Residue	180-195°/0·5

Pyrolyses

7.5.3: 41-42, Allyl acetate (XVIII).
7.6.1: 43, Ethylene (V).
7.6.2: 44, Benzoic acid (XIX).

Pyr. No.	41	42	43	44
Reactor	2	3	5	3
Temperature	500°	500°	500°	500°
Amt. pyr'd	60 g.	50 g.	8.5 l.	32 g.
Pyrolysate	50 5 g.	42 5 g.		31 g.
Gas pyr'sate	7 l.	4.5 l.	8.5 l.	ca. 50 ml.
Rate, g./min.	1.0	0.62	0.135	0.64
t_c seconds	4.7	4.6	ca. 9.8	5.3
Gas Analysis:				
CO_2	51 %	43.7 %	-	
CO	43	47.0	-	
C_nH_{2n}	6	9.3	50.5 %	
H_2	-	-	32.9	
CH_4/C_nH_{2n+2}	-	-	16.6	
Pyrolysate Fractions:				
amount	1 g.			
F1	45-70°/760			
amount	2 g.			
F2	70-102°/750			
amount	6 g.			
F3	70-100°/760			
amount	32.5 g.			
F4	100-108°/760			
amount	4 g.			
F5	Residue			

7.8 : Appendix on Experimental Methods of Analysis.

7.8.1 : Paper chromatographly with a Stationary Liquid Phase.

The method of paper chromatography proposed by Burton (88) has been applied with considerable success to separate the 2:4-dinitrophenylhydrazones of acetophenone and 4-acetylbenzoic acid. Hitherto it had been found to be virtually impossible to effect any separation at all using the standard methods of paper chromatography.

This method consists of using a standard grade of paper (Whatman's No. 1) pretreated with the aqueous solution of an ester of an hydroxy acid. This acts as the stationary phase, and suitable esters are ethyl lactate (70 % in water) and ethyl tartrate (in methanol and water). The chromatogram is developed in light petroleum reinforced with a solvent such as carbon tetrachloride.

In practice it was found that ethyl tartrate gave the best results, the solution being made up as follows, ethyl tartrate : water : methanol :: 5 : 15 : 60. The paper is immersed in this solution, drained, and then allowed to become surface dry in a gentle current of air. The test spots are applied, and then developed by the descending technique in a tank presaturated with the solvent mixture. For the first exploratory runs, petroleum (b. 60-80^{o}) reinforced with 2 % carbon tetrachloride was used, but later it was found better

to reinforce the petroleum with 20 % acetone.

The developed chromatograms can generally be analysed with the unaided eye, but they are seen to best advantage when viewed under ultra-violet light. Under this light the actual centres of concentration of the spots become clearly visible, and quite small traces can be detected. The test was not regarded as conclusive until it had been repeated and shown to be reproducible.

7.8.2 : Nitroprusside Test for Methyl Ketones (110).

This test has been used in pyrolysis 23 to demonstrate the presence of acetophenone in the pyrolysate of 4-acetylbenzoic acid. The test is carried out by placing a drop of the aqueous or alcoholic test solution on a spotting plate and then adding a drop of 5 % aqueous sodium nitroprusside and a drop of 30 % aqueous sodium hydroxide. After a short time a colour develops, and this may be taken as the test, or the solution may be acidified with glacial acetic acid with a resultant further colour change. In this example the colour at the alkaline stage was more definitive. Synthetic mixtures were prepared and used for comparison.

7.8.3 : Alkali-Alkyl Xanthate Test for Alcohols (111).

This test has been used in pyrolysis 41 to discover whether any alcohols were present in the pyrolysate from allyl acetate. A drop of the test solution is placed in a small test tube

along with a drop of carbon disulphide and a small amount of solid sodium hydroxide. The mixture is shaken for 5 minutes, whereupon 2 drops of 1 % ammonium molybdate solution are added, and, as soon as the alkali has dissolved, the solution is carefully acidified with 2N sulphuric acid. This is shaken, and 2 drops of chloroform added. When primary or secondary alcohols are present, the chloroform layer is coloured violet. Since esters may give a positive reaction because of hydrolysis, only a negative result in such a case has real significance.

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